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This report describes the results and the progress we have made in the study of: (a) Impurity-induced layer disordering (IILD) of thin layer III-V heterostructures and its application to quantum well heterostructure lasers, (2) the fundamental behavior of quantum well heterostructures and the application of IILD to laser devices, and (3) the continuous (cw) room temperature (300 K) laser operation of $Al_xGa_{1-x}As$-GaAs quantum well heterostructures grown on Si.

Silicon

Aluminum Gallium Arsenide
Gallium Arsenides! (mgm)

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donor (Si) IILD, acceptor (Zn) IILD, IILD QWH lasers, capping (SiO_2, Si_3N_4) effect on IILD, IILD with As-rich annealing, IILD with Ga-rich annealing, Fermi-level effect on IILD, QWH lasers on Si, visible-spectrum QWH lasers, IILD reduction of dislocations in GaAs-on-Si.

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THE CONSTRUCTION AND STUDY OF IMPROVED $Al_xGa_{1-x}As$-GaAs HETEROSTRUCTURE DEVICES

FINAL REPORT
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December, 1988

U.S. ARMY RESEARCH OFFICE
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ABSTRACT

This report describes the results and the progress we have made in the study of: (1) Impurity-induced layer disordering (IILD) of thin layer III-V heterostructures and its application to quantum well heterostructure lasers, (2) the fundamental behavior of quantum well heterostructures and the application of IILD to laser devices, and (3) the continuous (cw) room temperature (300 K) laser operation of $Al_xGa_{1-x}As$-GaAs quantum well heterostructures grown on Si.

I. INTRODUCTION

During the course of this project we have been interested in the properties, in general, of III-V semiconductor quantum well heterostructures (QWHs). Specifically, we have been interested in a broader range of QWH lasers and in more advanced forms of QWH lasers. Besides the advantageous fundamental properties of QWHs (two-dimensional properties), the ultra-thin layered form of QWHs offers another major advantage: Quantum-well thin layers can be selectively intermixed, by impurity induced layer disordering (IILD), to form higher gap bulk layers. For example, simply by photolithography and diffusion processing, we can render a large uniform $Al_xGa_{1-x}As$-GaAs QWH wafer into single-stripe or multiple-stripe buried heterostructure lasers or, indeed, into arbitrary patterns. There is no doubt that IILD can be used for a wide range of integrated electronic-optoelectronic structures, most of which remain to be developed. Because IILD is so important fundamentally as well as practically, and is, moreover, peculiarly suited to study and application on QWH's, we have expended major effort on the combined study of QWHs and IILD.

As this project has developed, we have published or given meeting reports on all substantial results. Since we have decribed all of the work of prior years in earlier reports, specifically detailed journal publications, here we merely list all of the work of 1988 (and beyond) as references, and append titles and abstracts of 1988 (and 1989) journal articles in order to supply more detailed information. Note that some of this work has received also some other support, e.g., MRL (NSF) analytical support and ERC (NSF) support on crystal growth. In addition, we have received some industrial support in the form of special crystals. We mention that indeed much of our work has been

carried out with individuals in various U. S. industrial laboratories (Shichijo, Texas Instruments; Epler, Xerox; Burnham, Amoco; Craford, et al., Hewlett-Packard; Ludowise, Hewlett-Packard, Gavrilovic, et al., Polaroid). Hence, in this work "technolgy transfer" has been built-in automatically.

II. ACCOMPLISHMENTS

The reference section of this report, by way of paper titles and abstracts, describes the progress we have made in three main areas of work: (1) impurity-induced layer disordering (IILD), (2) study of quantum-well heterostructures (QWHs) and their application to laser devices, and (3) continuous (cw) room temperature (300 K) laser operation of $Al_xGa_{1-x}As$-GaAs QWHs grown on Si.

A. Impurity-Induced Layer Disordering (IILD)

In the time since we introduced IILD in late 1980 and first reported it in 1981, interest in IILD has developed world wide, and a considerable journal literature on IILD has developed. Besides making extensive contributions to the study of IILD (see Refs. 1, 2, 3, 5, 7, 10, 11, 12, 17, 18, 22, 24, 27), we have prepared an extensive review of IILD and its use (Ref. 18). The areas in which we have made recent contributions to IILD are:

(1) We have studied diffusion and disordering mechanisms and have established the importance of the Fermi-level location (Refs. 2, 7, 12, 17, 18, 24) in IILD, the so-called Fermi-level effect.

(2) The importance in IILD of the crystal surface capping (Si, SiO_2, Si_3N_4) and the control of the thermal anneal ambient (Column-III or Column-V rich conditions) has been elucidated (Refs. 1, 7, 12, 17, 18, 22, 24, 27).

(3) Other means of layer disordering than just the use of Si diffusion or Zn diffusion (or implantation) have been studied, e.g., Ge diffusion from the vapor (Ref. 5) and combined Si-oxygen diffusion (which compensates the effect of the Si donor, Ref. 27).

(4) By examining IILD in the heterosystem $In_y(Al_xGa_{1-x})_{1-y}P$-$In_yGa_{1-y}P$-GaAs ($y \approx 0.5$), we have shown that IILD proceeds mainly via exchange of Column III atoms (Refs. 10, 17, 18).

(5) We have used IILD studies to develop a better understanding of how impurity diffusion proceeds in GaAs (Refs. 2, 12, 17, 18, 22).

(6) Because atom motion, and hence defect motion (or the opposite), is involved in IILD, we have employed IILD for dislocation reduction in GaAs grown on Si (Ref. 11), as well as to disorder the ordered form of InGaAsP (Ref. 19), GaAsP (Ref. 19), GaInP (Ref. 21), and AlGaInP (Ref. 21).

B. Quantum-Well Heterostructure (QWH) Lasers

An important aspect of IILD is, of course, that it has application in forming buried heterostructure single-stripe and multiple-stripe lasers. In a number of the papers we have published dealing with the fundamental properties of IILD, we have also described the use of IILD to fabricate high performance buried heterostructure lasers (simply by crystal processing and not regrowth procedures). Some of these results appear in Refs. 3, 5, 7, 18, 27.

As part of our interst in QWHs, and in IILD, we have broadened our work beyond the $Al_xGa_{1-x}As$-GaAs heterosystem, including to the short wavelength system $In_{0.5}(Al_xGa_{1-x})_{0.5}P$-GaAs. As already mentioned, we have used $In_{0.5}(Al_xGa_{1-x})_{0.5}P$-GaAs for IILD studies (e.g., Ref. 10), and, even more important, to demonstrate short wavelength cw 300 K QWH lasers, both via photopumping (Refs. 9, 20) and as diodes ($\lambda \lesssim 6400$ Å, Refs. 15 and 25). With the exception of $In_{0.5}(Al_xGa_{1-x})_{0.5}P$-GaAs, there are not many heterosystems that can achieve short wavelength laser operation, which has obvious importance. $In_{0.5}(Al_xGa_{1-x})_{0.5}P$-GaAs is not inherently a matched system, but we know (Ref. 25) from -30°C laser operation ($\sim$ 6350 Å, $\lesssim$ 12 mW) at quantum efficiencies $\eta \lesssim 30\%$ that this III-V system can eventually replace the He-Ne laser (and probably be applied much more broadly).

As a final part of our study of stimulated emisison in QWHs, we have returned to the problem of the phonon-assisted laser operation of QWHs: does it or doesn't it occur? We have supplied the answer (positive!) to this ten year old question, and demonstrate the importance of high-Q versus low-Q heat sinking for photopumping of QWH samples (Ref. 26).

C. Continuous 300 K Quantum Well Lasers on Si

Even though the problem of growing (constructing) cw 300 K $Al_xGa_{1-x}As$-GaAs lasers on Si has received worldwide attention, including in many leading U.S. and Japanese laboratories, to the best of our knowledge very little in improved performance has been achieved beyond the cw 300 K lasers we reported well over one year ago. This indicates the nature of the mismatch problems (lattice and thermal coefficient of expansion) and the over-estimation in many

quarters of how quickly major problems can be solved. Although in the past year there has been little reported of improvements in lasers on Si, actually quite a bit has been learned about these devices. For example, we have demonstrated and reported at the 1988 IEEE Device Research Conference (June, 1988, Boulder) that one of the expected advantages of constructing $Al_xGa_{1-x}As$-GaAs QWH lasers on Si is indeed correct. In comparison with similar lasers grown on GaAs substrates, the QWH lasers on Si, when heat sunk from the substrate side, exhibit better heat removal (lower thermal resistance) than the case of similar heat removal via a GaAs substrate (Ref. 14). This is important if semiconductor lasers are ever to be operated, active-region side mounted upward, in array configurations where individual lasers (with other devices, e.g., transistors and detectors) are addressable and thus can be made part of some form of integrated structure (optoelectronic IC or electronic-photonic IC). As limited as is the present performance (cw 300 K) of $Al_xGa_{1-x}As$-GaAs QWH lasers grown on Si, the fact that Si affords a better heat sink than does a GaAs substrate is ultimately one of the more important reasons to be concerned with the problem of GaAs-on-Si. Also, we note that our $Al_xGa_{1-x}As$-GaAs QWH lasers grown on Si are much longer lived than the original (1970) cw 300 K $Al_xGa_{1-x}As$-GaAs double heterojunction lasers. This too offers some reason for optimism in this area of work.

It is well known that if the combination of GaAs and $Al_xGa_{1-x}As$ layers grown on a Si substrate exceeds a total thickness of ~ 5 μm, microcracks (e.g., <110> cleave lines on a {100} substrate) develop in the epitaxial material. From one point of view this can be regarded as a serious problem, but from another viewpoint this can be a mechanism for strain relief. Because

of the lattice mismatch between GaAs (or $Al_xGa_{1-x}As$) and Si, at the epitaxial layer growth temperature dislocations form to accommodate the difference in lattice size. When the III-V layers are cooled from the growth temperature to room temperature, they contract much more than the Si substrate, and, if they are beyond a certain critical thickness ($\sim 5\ \mu m$), they cleave in tension to accommodate the greater contraction of the GaAs than the Si. Generally speaking this is a problem. Microcracks are not normally desired in devices, and, of course, in some cases must be suppressed or eliminated.

From another viewpoint, however, a microcrack is a mechanism to relieve the strain caused by lattice mismatch, and maybe devices can be built near microcracks, particularly if the microcracks are introduced in a pattern or regular geometry. The reason to require that microcracks fit (eventually) a pattern is, clearly, to permit construction of a regular array of devices as in some form of integrated circuit. We already have data indicating that microcracks can play a significant role in the behavior of cw 300 K $Al_xGa_{1-x}As$-GaAs QWH lasers grown on Si (Ref. 13). Not only can microcracks help relieve the mismatch strain of GaAs-on-Si, they can, in fact, traverse the entire length of the active region of a QWH stripe geometry laser on Si without harm (Ref. 13). Also, they can be located at right angles to a laser stripe, thus creating a useful form of compound cavity (Ref. 13). In other words, microcracks are not necessarily all bad and may become an important part of some GaAs-on-Si devices.

III. CONTRIBUTORS

The principal investigators contributing to various parts of the work

reported here are:

1) N. Holonyak, Jr. (Refs. 1-27)

2) G. E. Stillman (Refs. 6, 8)

(This report has been prepared by N. Holonyak, Jr.) The graduate students either receiving direct project support or otherwise contributing to various portions of the work reported here are:

1) J. M. Dallesasse, Ph.D. Student

2) D. G. Deppe, Ph.D. Student (Shell-Fellowship)

3) D. C. Hall, Ph. D. Student

4) G. S. Jackson, Ph.D. Student

5) F. Kish, Ph.D. Student

6) J. S. Major, Jr., Ph. D. Student

7) D. W. Nam, Ph. D. Student (Kodak Fellowship)

8) M. A. Plano, Ph.D. Student (Stillman advisor)

9) W. E. Plano, Ph.D. Student

10) E. J. Vesely, Ph. D. Student (NSF Fellowship)

Note that some of the graduate students making contibutions to this work Refs. 1-27) have received support from other projects or have received fellowship support. G. S. Jackson (Refs. 3, 4, 8, and 16) has completed his Ph.D. (Spring 1988) and is employed in GaAs device work at Raytheon, Boston. Another contributor to this work, D. G. Deppe, has completed his Ph.D.

(October, 1988) and is now employed at A.T.&T. Bell laboratories (Murray Hill, NJ). A third contributor, L. J. Guido, has also completed his Ph.D. work (November, 1988) and now has a post-doctoral appointment (same project). In the period of this work W. E. Plano and D. W. Nam have completed their Ph.D. preliminary examinations. As already mentioned, the National Science Foundation Engineering Research Center has supported much of our MOCVD crystal growth (EMCORE reactor) and our NSF MRL has supported our TEM and SIMS analyses, which are spread throughout much of the work reported here.

REFERENCES

1. L.J. Guido, W.E. Plano, D.W. Nam, N. Holonyak, Jr., J.E. Baker, R.D. Burnham, and P. Gavrilovic, "Effect of Surface Encapsulation and As_4 Overpressure on Si Diffusion and Impurity-Induced Layer Disordering in GaAs, $Al_xGa_{1-x}As$, and $Al_xGa_{1-x}As$-GaAs Quantum Well Heterostructures," J. Electron. Mater. 17, 53-56 (Jan, 1988).

2. D.G. Deppe, N. Holonyak, Jr., and J.E. Baker, "Sensitivity of Si Diffusion in GaAs to Column IV and VI Donor Species," Appl. Phys. Lett. 52, 129-131 (11 Jan, 1988).

3. L.J. Guido, G.S. Jackson, D.C. Hall, W. E. Plano, and N. Holonyak, Jr., "Carbon-Doped $Al_xGa_{1-x}As$-GaAs Quantum Well Lasers," Appl. Phys. Lett. 52, 522-524 (15 Feb, 1988).

4. G.S. Jackson, D.C. Hall, L.J. Guido, W.E. Plano, N. Pan, N. Holonyak, Jr., and G.E. Stillman, "High-Power Gain-Guided Coupled-Stripe Quantum Well Laser Array By Hydrogenation," Appl. Phys. Lett. 52, 691-693 (29 Feb, 1988).

5. D.G. Deppe, W.E. Plano, J.M. Dallesasse, D.C. Hall, L.J. Guido, and N. Holonyak, Jr., "Buried Heterostructure $Al_xGa_{1-x}As$ Quantum Well Lasers by Ge Diffusion From the Vapor," Appl. Phys. Lett. 52, 825-827 (7 March, 1988).

6. M.A. Plano, W.E. Plano, M.A. Haase, S.S. Bose, N. Holonyak, Jr., and G.E. Stillman, "Generation of an Anomalous Hole Trap in GaAs by As Overpressure Annealing," Appl. Phys. Lett. 52, 1077-1079 (28 March, 1988).

7. D.G. Deppe, L.J. Guido, and N. Holonyak, Jr., "Impurity-Induced Layer Disordering in $Al_xGa_{1-x}As$-GaAs Quantum Well Heterostructures," 1988 MRS Spring Meeting (Reno, 5-9 April, 1988), Matls. Res. Soc. Symp. Proc. 126, 31-42 (1988).

8. N. Pan, M.S. Feng, G.S. Jackson, S.S. Bose, L.J. Guido, N. Holonyak, Jr., and G.E. Stillman, "Hydrogenation of GaAs and Application to Device Processing," 1988 MRS Spring Meeting, (Reno, 5-9 April, 1988), Matls. Res. Soc. Symp. Proc. 126, 257-263 (1988).

9. D.W. Nam, D.G. Deppe, N. Holonyak, Jr., R.M. Fletcher, C.P. Kuo, T.D. Osentowski, and M.G. Craford, "Short Wavelength ($\sim$625 nm) Room Temperature Continuous Laser Operation of $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ Quantum Well Heterostructures," Appl. Phys. Lett. 52, 1329-1331 (18 April, 1988).

10. D.G. Deppe, D.W. Nam, N. Holonyak, Jr., K.C. Hsieh, J.E. Baker, C.P. Kuo, R.M. Fletcher, T.D. Osentowski, and M.G. Craford, "Impurity-Induced Layer Disordering in High Gap $In_y(Al_xGa_{1-x})_{1-y}P$ Heterostructures," Appl. Phys. Lett. 52, 1413-1415 (25 April, 1988).

11. D.G. Deppe, N. Holonyak, Jr., K.C. Hsieh, D.W. Nam, W.E. Plano, R.J. Matyi, and H.Shichijo, "Dislocation Reduction by Impurity Diffusion in Epitaxial GaAs Grown on Si," Appl. Phys. Lett. 52, 1812-1814 (23 May, 1988).

12. D.G. Deppe, N. Holonyak, Jr., W.E. Plano, V.M. Robbins, J.M. Dallesasse, K.C. Hsieh, and J.E. Baker, "Impurity Diffusion and Layer Interdiffusion in $Al_xGa_{1-x}As$-GaAs Heterostructures," J. Appl. Phys. 64, 1838-1844 (15 Aug, 1988).

13. D.G. Deppe, D.C. Hall, N. Holonyak, Jr., R.J. Matyi, H. Shichijo, and J.E. Epler, "Effects of Microcracking on $Al_xGa_{1-x}As$-GaAs Quantum Well Lasers Grown on Si," Appl. Phys. Lett. 53, 874-876 (5 Sept, 1988).

14. D.C. Hall, D.G. Deppe, N. Holonyak, Jr., R.J. Matyi, H. Shichijo, and J.E. Epler, "Thermal Behavior and Stability of Room Temperature Continuous $Al_xGa_{1-x}As$-GaAs Quantum Well Heterostructure Lasers Grown on Si," J. Appl. Phys. 64, 2854-2860 (15 Sept 1988).

15. J.M. Dallesasse, D.W. Nam, D.G. Deppe, N. Holonyak, Jr., R.M. Fletcher, C.P. Kuo, T.D. Osentowski, and M.G. Craford, "Short-Wavelength ($\lesssim$ 6400 Å) Room Temperature Continuous Operation of p-n $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ Quantum Well Lasers," Appl. Phys. Lett. 53, 1826-1828 (7 Nov 1988).

16. G.S. Jackson, J. Beberman, M.S. Feng, K.C. Hsieh, N. Holonyak, Jr., and J. Verdeyen, "Damaged and Damage-Free Hydrogenation of GaAs: The Effect of Reactor Geometry," J. Appl. Phys. 64, 5175-5178 (15 Nov 1988).

17. D.G. Deppe, W.E. Plano, J.E. Baker, N. Holonyak, Jr., M.J. Ludowise, C.P. Kuo, R.M. Fletcher, T.D. Osentowski, and M.G. Craford, "Comparison of Si_{III}-Si_V and Si_{III}-V_{III} Diffusion Models in III-V Heterostructures Lattice Matched to GaAs," Appl. Phys. Lett. 53, 2211-2213 (28 Nov 1988).

18. D.G. Deppe and N. Holonyak, Jr., "Atom Diffusion and Impurity-Induced Layer Disordering in Quantum Well III-V Semiconductor Heterostructures," J. Appl. Phys. 64, R93-R113 (15 Dec 1988).

19. W.E. Plano, D.W. Nam, K.C. Hsieh, and N. Holonyak, Jr., "Column III and V Ordering in InGaAsP and GaAsP Grown on GaAs by Metalorganic Chemical Vapor Deposition," Appl. Phys. Lett. 53, 2537-2539 (19 Dec 1988).

20. C.P. Kuo, R.M. Fletcher, T.D. Osentowski, M.G. Craford, D.W. Nam, N. Holonyak, Jr., K.C. Hsieh, and J.E. Fouguet, "Stimulated Emission in $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ Quantum Well Heterostructures," 4th International Conference on Metalorganic Vapor Phase Epitaxy, May 16-20, 1988, Hakone, Japan, J. Crystal Growth 93, 389-395 (Nov/Dec 1988).

21. P. Gavrilovic, F.P. Dabkowski, K. Meehan, J.E. Williams, W. Stutius, K.C. Hsieh, N. Holonyak, Jr., M.A. Shahid, and S. Mahajan, "Disordering of the Ordered Structure In MOCVD-Grown GaInP and AlGaInP by Impurity Diffusion

and Thermal Annealing," 4th International Conference on Metalorganic Vapor Phase Epitaxy, May 16-20, 1988, Hakone, Japan, J. Crystal Growth 93, 426-433(Nov/Dec 1988).

22. L.J. Guido, N. Holonyak, Jr., K.C. Hsieh, and J.E. Baker, "Depth-Dependent Native Defect-Induced Layer Disordering in $Al_xGa_{1-x}As$-GaAs Quantum Well Heterostructures," Appl. Phys. Lett. 54, (16 Jan 1988).

23. K.C. Hsieh, M.S. Feng, G.E. Stillman, N. Holonyak, Jr., C.R. Ito, and M. Feng, "Hydrogenation and Subsequent Hydrogen Annealing on GaAs on Si," Appl. Phys. Lett. 54, (23 Jan 1989).

24. L.J. Guido, N. Holonyak, Jr., and K.C. Hsieh, "Role of Native Defects in Al-Ga Interchange and Layer Disordering in $Al_xGa_{1-x}AsAs$ Quantum Well Heterostructures," Conf. on GaAs and Related Compounds, Atlanta, 11-14 Sept, 1988, in , editor (Inst. Phys. Conf. Series, No. , Bristol, 1989), pp. .

25. R.M. Fletcher, C.P. Kuo, T.D. Osentowski, M.G. Craford, D.W. Nam, J.M. Dallasasse, and N. Holonyak, Jr., "CW Room Temperature Operation (<640 nm) of AlGaInP Multi-Quantum-Well Lasers," Conf. on GaAs and Related Compounds, Atlanta, 11-14 Sept, 1988, in , editor (Inst. Phys. Conf. Series, No. , Bristol, 1989), pp. .

26. N. Holonyak, Jr., D.W. Nam, W.E. Plano, E.J. Vesely, and K.C. Hsieh, "Observation of Phonon-Assisted Laser Operation of $Al_xGa_{1-x}As$-GaAs Quantum Well Heterostructures," Appl. Phys. Lett. 54, (1989).

27. L.J. Guido, J.S. Major, Jr., J.E. Baker, N. Holonyak, Jr., and R.D. Burnham, "Disorder-Defined Buried Heterostructure $Al_xGa_{1-x}As$-GaAs Quantum Well Lasers by Diffusion of Silicon and Oxygen From Al-Reduced SiO_2," Appl. Phys. Lett., submitted.

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Effect of Surface Encapsulation and As_4 Overpressure on Si Diffusion and Impurity-Induced Layer Disordering In GaAs, $Al_xGa_{1-x}As$, and $Al_xGa_{1-x}As$-GaAs Quantum Well Heterostructures

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Data are presented demonstrating that the surface encapsulant and the As_4 overpressure strongly affect Si diffusion in GaAs and $Al_xGa_{1-x}As$, and thus are important parameters in impurity-induced layer disordering. Increasing As_4 overpressure results in an *increase* in diffusion depth in the case of GaAs, and a *decrease* in diffusion depth for $Al_xGa_{1-x}As$. In addition, the band-edge exciton is observed in absorption on an $Al_xGa_{1-x}As$-GaAs superlattice that is diffused with Si and is converted to bulk crystal $Al_yGa_{1-y}As$ via impurity-induced layer disordering. In contrast, the exciton is not observed in absorption on GaAs diffused with Si in spite of the high degree of compensation. These data indicate that the Si diffusion process, and the properties of the diffused material, are different for GaAs and for $Al_xGa_{1-x}As$-GaAs superlattices converted into uniform $Al_yGa_{1-y}As$ ($0 \le y \le x \le 1$) via impurity-induced layer disordering with the amphoteric dopant Si.

Key words: Si diffusion, impurity-induced layer disordering, $Al_xGa_{1-x}As$-GaAs superlattice, exciton absorption.

INTRODUCTION

Since the demonstration that an extrinsic impurity, *e.g.*, Zn,[1] can be used to enhance the layer intermixing (*i.e.* disordering) of an $Al_xGa_{1-x}As$-GaAs quantum well heterostructure (QWH), impurity-induced layer disordering (IILD) has proven to be an important tool for constructing sophisticated forms of buried QWH lasers.[2-4] As with other, more developed, integrated circuit technologies IILD is used to selectively modify the as-grown properties (band-gap, refractive index) of an $Al_xGa_{1-x}As$-GaAs heterostructure in the two-dimensional plane of the epitaxial layers. Consequently, this newer form of "band-gap engineering" is ideally suited for use in the construction of optoelectronic integrated circuits (OEICs).

Because of the increased interest in the application of IILD to OEIC processing, attempts have been made to model the enhancement of Al-Ga interchange in the presence of extrinsic impurities.[5,6] Independent of the details of these models, it is clear that native defects, *e.g.* vacancies, play a crucial role in the Al-Ga interchange process. Further investigation is required to determine the effect of the surface encapsulant, the crystal Fermi level, and the $Al_xGa_{1-x}As$-GaAs interfaces on the concentration, mobility, and charge state of the native defects. In this paper data are presented demonstrating that the surface encapsulant and As_4 overpressure (p_{As_4}) strongly affect Si diffusion in GaAs and $Al_xGa_{1-x}As$, and thus are important parameters in layer disordering.[7] The data show that increasing p_{As_4} results in an increase in diffusion depth in the case of GaAs, and a decrease in diffusion depth for $Al_xGa_{1-x}As$. These trends suggest that the Si diffusion process, which is one of the more important methods for IILD, and the properties of the diffused material are different for GaAs and for bulk-crystal $Al_yGa_{1-y}As$ formed by IILD of $Al_xGa_{1-x}As$-GaAs superlattices. This conclusion is further supported by the fact that we observe the band-edge exciton in absorption for a Si-diffused and layer-disordered $Al_xGa_{1-x}As$-GaAs superlattice (SL), but not for Si-diffused GaAs.

EXPERIMENTAL PROCEDURE

The epitaxial layers used in these experiments, which are grown via metalorganic chemical vapor

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Ref. 2

Sensitivity of Si diffusion in GaAs to column IV and VI donor species

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Secondary ion mass spectroscopy and carrier concentration measurements are used to characterize Si diffusion into GaAs wafers containing two fundamentally different forms of donors, the column IV donors Si or Sn and the column VI donors Se or Te. A decrease in the Si diffusion rate is found in GaAs containing the column VI donors compared to the column IV donors. This trend is consistent with the model in which the Si diffuses as donor-gallium-vacancy complexes. The decrease in the Si diffusion coefficient is attributed to the greater binding energy of column VI donor-gallium-vacancy nearest-neighbor complexes, thus reducing the concentration of free-gallium vacancies available to complex with the Si.

Although donor diffusion into GaAs or $Al_xGa_{1-x}As$ is typically more difficult and less common than acceptor diffusion, Si serves as an important donor that can be diffused and can be used in device fabrication. The Si diffusion coefficient is "fast" enough so that reasonable annealing times and temperatures can be used, and also it readily diffuses into the crystal without significant alloying problems at the crystal surface.[1-4] In addition, the Si impurity greatly enhances layer interdiffusion at $Al_xGa_{1-x}As$-GaAs heterointerfaces,[4] which is a maskable and thus selective process that has made possible fabrication of low threshold buried heterostructure $Al_xGa_{1-x}As$-GaAs quantum well (QW) lasers.[5-7] It is likely also that the impurity-induced layer-disordering property will find other applications in integrated optoelectronic devices. To realize fully the potential of the layer intermixing process, and the resulting shift from QW lower gap to bulk-crystal higher gap, will require a detailed understanding of the Si diffusion mechanism as well as the crystal properties that control the diffusion. Although Si has been proposed to diffuse in GaAs by Si_{Ga}^{+}-Si_{As}^{-} neutral pairs hopping to neighboring As and Ga vacancies,[3] the diffusion rate is, in fact, strongly controlled by the Ga vacancy concentration generated at the crystal surface during the diffusion.[1-3] Based on this and the strong dependence that Si diffusion has on the background concentration of *p*-type impurity in the crystal, we recently have suggested that the Si diffuses instead by means of the Si_{Ga}^{+} donor and the ionized Ga vacancy V_{Ga}^{-} (or V_{Ga}^{--}, etc.) complex, which makes the Si diffusion Fermi-level dependent.[8] Note that the Fermi level will not only control the charge state of a deep level such as V_{Ga},[9] but will also control its solubility in the crystal.[10] In this letter we report data on the diffusion of Si into GaAs that contains varying amounts of several fundamentally different donor impurities, specifically either the column IV donors Si or Sn, or the column VI donors Se or Te, and in one case (for reference) the acceptor impurity Zn. The experimental data, with the large dependence on donor species, are consistent with the argument that the Si diffuses in GaAs as the complex Si_{Ga}-V_{Ga}.

The GaAs wafers used in this study are oriented ⟨111⟩, and the Si is diffused into the As-rich surface. Polished wafers are first etched in 5:1:1 H_2SO_4:H_2O_2:H_2O for 5 min and then rinsed in de-ionized water and blown dry under a N_2 stream. The wafers are then etched in NH_4OH for 5 min, again rinsed in de-ionized water and dried, and then immediately loaded into an *e*-beam evaporation system in which a ~250-Å-thick layer of Si is deposited on the surface of the wafers. The wafers are then sealed in an evacuated quartz ampoule (2.5 cm^3 volume) along with a piece of clean elemental As weighing 30–40 mg. The anneals are performed for 10 h at 815 °C, after which secondary ion mass spectroscopy (SIMS) is used to analyze the Si diffusion profiles in the GaAs wafers. The carrier concentration is also measured using a Polaron 4200 *C-V* measurement system. The Si diffusion profile can depend on surface preparation of the GaAs wafer, layer thickness of the evaporated Si source, and the As overpressure on the annealing wafer. Therefore, comparisons are made on wafers processed simultaneously and then annealed simultaneously in the same ampoule.

Figure 1 shows the results of SIMS analysis on wafers with background doping varying from: (a) *p*-type, $n_{Zn} = 5\times10^{18}$ cm^{-3}; to (b) low doping, $n_{Sn} = 10^{16}$ cm^{-3}; to (c) *n*-type, $n_{Sn} = 3\times10^{18}$ cm^{-3}. Two trends can be seen in the data of Fig. 1. The first is that as the background doping

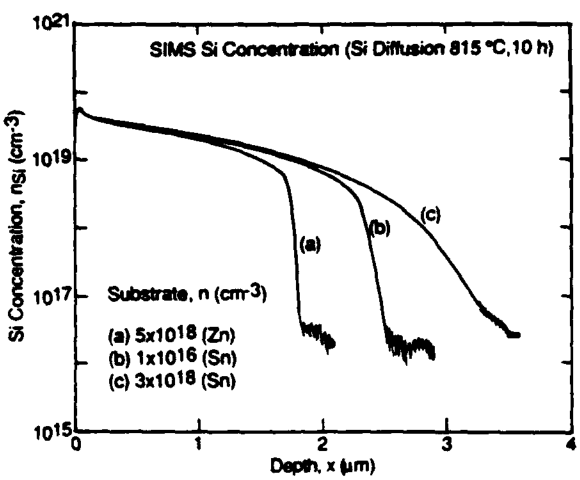

FIG. 1. SIMS profiles for Si diffusion at 815 °C (10 h) into GaAs of different background doping species and concentrations. The Si diffusion depth increases and the diffusion front becomes less steep as the background doping in the wafer changes from: (a) *p*-type, $n_{Zn} = 5\times10^{18}$ cm^{-3}; to (b) low doping, $n_{Sn} = 10^{16}$ cm^{-3}; to (c) *n*-type, $n_{Sn} = 3\times10^{18}$ cm^{-3}.

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Carbon-doped $Al_xGa_{1-x}As$-GaAs quantum well lasers

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Data are presented demonstrating that carbon (C) can be used as the active *p*-type dopant in high-quality $Al_xGa_{1-x}As$-GaAs quantum well laser crystals. We show, by fabricating three different types of stripe geometry laser diodes (oxide stripe, hydrogenated stripe, and impurity-induced layer-disordered stripe), that C is a stable dopant and compatible in behavior with typical integrated-circuit style of device processing. The data suggest that more complicated laser geometries are possible on C-doped material because of minimal pattern "undercutting" after processing by, for example, hydrogenation or impurity-induced layer disordering.

Recent work has demonstrated that the incorporation (via diffusion, implantation, or even epitaxial growth) of various impurities into $Al_xGa_{1-x}As$-GaAs heterostructure devices can result in considerable layer intermixing, i.e., impurity-induced layer disordering (IILD).[1-3] Unintentional heterointerface disordering is not desired, for example, in devices that rely on reduced dimensionality for improved performance. In contrast, intentional and selective IILD (i.e., "band-gap engineering" in the plane) have been used to enhance device performance (e.g., buried heterostructure quantum well lasers).[4-7] In view of these developments, it is important to investigate alternatives to the dopants that are typically used (Be, Si) in molecular beam epitaxy (MBE) and that are used (Zn, Mg, Se) in metalorganic chemical vapor deposition (MOCVD) of GaAs and $Al_xGa_{1-x}As$. Several considerations in evaluating an alternative dopant are: (1) the device performance of the as-grown crystal, (2) the dopant stability relative to processing operations (heating), and (3) the compatibility of the dopant with standard integrated-circuit (IC) style of processing, e.g., the conductivity type change of IILD. Data presented in this letter demonstrate that carbon, which is usually regarded as just a background contaminant, can be employed as the active *p*-type dopant in a variety of stripe geometry $Al_xGa_{1-x}As$-GaAs quantum well (QW) lasers.

The crystals used in these experiments are grown via MOCVD[8] in an EMCORE GS 3000 reactor. Host crystal atoms are provided via the metalorganics trimethylaluminum (TMAl) and trimethylgallium (TMGa), and the hydride arsine (AsH_3, 100%). The *p*-type dopant sources are carbon (C), a by-product of the TMAl and TMGa pyrolysis reactions, and magnesium (MCp_2Mg). The *n*-type dopant source is hydrogen selenide (H_2Se). The $Al_xGa_{1-x}As$-GaAs QW laser crystal consists of the following epitaxial layers: an *n*-type GaAs buffer layer ($n_{Se} \sim 2\times10^{18}$ cm^{-3}, ~ 0.5 μm) grown directly on an *n*-type GaAs substrate ($n_{Si} \sim 2\times10^{18}$ cm^{-3}), followed by two *n*-type $Al_yGa_{1-y}As$($n_{Se} \sim 2\times10^{18}$ cm^{-3}, $y \sim 0.25$, 0.40) intermediate layers (~ 0.5 μm) to minimize the strain because of the lattice mismatch between the substrate and the succeeding high-gap $Al_xGa_{1-x}As$ ($x \sim 0.75$) active-region confining layers. The upper *p*-type ($n_C \sim 9\times10^{17}$ cm^{-3}) and lower *n*-type ($n_{Se} \sim 2\times10^{18}$ cm^{-3}) confining layers are each ~ 1 μm thick. The active region, grown directly after the lower confining layer, consists of an undoped $Al_{x'}Ga_{1-x'}As$ waveguide layer ($x' \sim 0.25$, 0.18 μm) with a ~ 140-Å GaAs QW in the center. Finally, the structure is capped with a thin GaAs layer ($n_{Mg} \sim 1\times10^{18}$ cm^{-3}, ~ 0.10 μm) for contact purposes. For laser diode fabrication the crystal is shallow diffused with Zn ($ZnAs_2$, 550 °C, 10 min, ~ 0.1 μm). The shallow contact diffusion increases the doping level in the *p*-type (Mg) contact layer so that nonalloyed ohmic contacts can be realized using standard Cr-Au metalization.

Earlier work has shown that C is the dominant residual acceptor in MBE or MOCVD GaAs.[9-11] However, much less is known about the properties of C as an active *p*-type dopant in GaAs or, more importantly, in $Al_xGa_{1-x}As$. A recent study of C incorporation in MOCVD $Al_xGa_{1-x}As$ shows that the C concentration increases both with Al mole fraction (x) and growth temperature (T_G),[12] which agrees with similar data (Fig. 1) of the present work. These data suggest that C can be employed as the active dopant in devices, which we demonstrate below on QW lasers. The Al mole fraction (x) in Fig. 1 is varied by simultaneously increasing the TMAl flow and decreasing the TMGa flow. The remaining growth conditions are held constant (growth rate

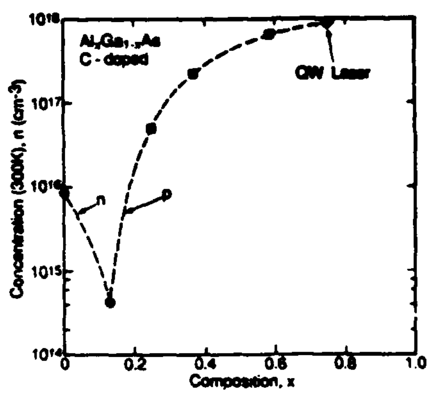

FIG. 1. Carrier concentration (300 K) in C-doped $Al_xGa_{1-x}As$ vs Al composition as determined via capacitance-voltage measurements (Hg probe). The Al composition values have been determined by double-crystal x-ray measurements. Data points denoted by solid circles (n type) and solid squares (p type) are taken from a set of calibration samples (growth rate ~ 11 μm/h, $T_G = 760$ °C, $P_G = 150$ Torr, V/III = 23). The hole concentration in the C-doped QW laser crystal (upper confining layer) is denoted by an arrow in the upper-right-hand corner (growth rate ~ 11 μm/h, $T_G = 825$ °C, $P_G = 150$ Torr, V/III = 48).

High-power gain-guided coupled-stripe quantum well laser array by hydrogenation

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High-power coupled-stripe (ten-stripe) $Al_xGa_{1-x}As$-GaAs quantum well lasers that are fabricated by hydrogenation are described. Continuous (cw) room-temperature thresholds as low as $I_{th} = 90$ mA and internal quantum efficiency as high as 85% are demonstrated. Continuous 300 K laser operation generating 2×375 mW (0.75 W) at 910 mA ($10I_{th}$) or 57% efficiency is described (8-μm-wide stripes on 12 μm centers). Minimal heating effects are observed up to the point of catastrophic failure.

The semiconductor laser has become an important and convenient source of high optical power. To overcome the problems of high-power emission (i.e., catastrophic facet damage and heating), large *p-n* junction areas are required and, of course, a uniform distribution of the injection current. This can be accomplished with an array of closely spaced active stripes. Optical coupling between very closely spaced laser stripes creates a narrowing of the far-field (FF) emission pattern and a corresponding increase in optical power density in the output beam.[1-3] Both gain-guided and index-guided laser arrays can be fabricated. Index-guided laser arrays are usually produced either by etching and some type of crystal regrowth,[4] or by layer disordering with an impurity (e.g., Zn or Si) in the case of an $Al_xGa_{1-x}As$-GaAs quantum well heterostructure (QWH).[5-7] Gain-guided laser arrays usually are fabricated by some form of current segregation at the contact layer. Shallow proton implants create highly resistive regions that channel current into the conducting stripes.[8] Insulators on the surface with stripe openings[2] and mesa stripes with Schottky-barrier contacts between them achieve similar results.[9] All of these schemes for gain-guided arrays allow significant current spreading at the stripe active regions, which is a limitation making gain-guided arrays vulnerable to gain-profile changes as operating conditions change. In fact, the current spreading is so large that usual gain-guided lasers can appear almost like broad-area devices.[9,10] A different form of gain-guided coupled-stripe laser array is described in this letter, a coupled-stripe array fabricated by hydrogen compensation of the dopants, i.e., hydrogenation. The hydrogenation process is effective in eliminating current spreading at the active region and allows broad area metallization over the entire *p* side, thus providing excellent heat sinking for high-power operation.

The coupled-stripe laser arrays described here are fabricated on a QWH crystal grown by metalorganic chemical vapor deposition (MOCVD) in an EMCORE GS 3000 reactor.[11] The separate confinement heterostructure (SCH) consists of a single 140-Å GaAs QW centered in an $Al_xGa_{1-x}As$ waveguide layer ($x\sim0.25$, 0.18 μm). The entire undoped active region is sandwiched between two $Al_{x'}Ga_{1-x'}As$ ($x'\sim0.75$, 1 μm) confining layers, the bottom one doped *n* type with Se ($n_{Se}\sim2\times10^{18}$ cm^{-3}) and the top doped *p* type with carbon (C) ($n_C\sim9\times10^{17}$ cm^{-3}). The use of C as a *p*-type dopant has been described elsewhere.[12] The fabrication of these laser diodes is similar to the process used previously for single stripe lasers.[13] Prior to the hydrogenation step a shallow Zn diffusion step (550 °C, 15 min), in a stripe array pattern, is carried out on the top-side GaAs contact layer to improve the *p*-side contact. The Zn-diffused regions are then masked with ~1000 Å of SiO_2, and the wafer is placed in a hydrogen plasma (750 Torr, 0.4 W/cm^2) at 250 °C for 8 min. Hydrogenation of the C in the nonmasked top regions creates highly resistive stripes in the *p*-type $Al_{0.75}Ga_{0.25}As$ confining layers.[12] After hydrogenation the oxide mask is removed, the wafer is thinned to ~100 μm thickness, and contacts (Ge-Au for *n* type, Cr-Au for *p* type) are evaporated onto the wafer. For cw operation the devices are mounted *p* side down on Cu heat sinks with In.

The laser array consists of ten 8-μm-wide *p*-type conducting stripes on 12 μm center-to-center spacing. A scanning electron micrograph of the ten-stripe wafer is shown in Fig. 1. Conventional *A-B* etch is used to stain the cleaved facet and enhance the contrast between the conducting and the resistive (4-μm-wide hydrogenated) *p*-type regions. In Fig. 1(a) no metallization is present, and the conducting stripes (8 μm wide) are completely etched down to the QW active region. This allows easy identification of the hydrogenated areas and the ten active stripes on 12 μm centers. The two outside stripes of the array are marked with vertical arrows 1 and 10 to denote the extent of the array. There appears to be little or no "undercutting" of the oxide mask in this device, which is in contrast to earlier results on single stripe lasers.[13] This difference may result from the use of C as the *p*-type dopant, as well as from confining the Zn diffusion to a stripe pattern. A metallized cleaved section is shown in Fig. 1(b) that also is stained with the *A-B* etch. The 8-μm-wide conducting stripes appear as dark regions separated by lighter (4 μm) hydrogenated areas. Again, the two vertical arrows in Fig. 1(b) point to the two laser stripes 1 and 10 at the edges of the array.

The results of pulsed operation of these ten-stripe lasers are summarized in Fig. 2. Excitation is by 5 μs pulses at a 10-kHz repetition rate. Diodes with different lengths are tested

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Buried heterostructure $Al_xGa_{1-x}As$-GaAs quantum well lasers by Ge diffusion from the vapor

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Data are presented on a method to diffuse Ge into quantum well $Al_xGa_{1-x}As$-GaAs crystals from a vapor source, thus effecting impurity-induced layer disordering, and shift from lower to higher gap. The Ge diffusion is characterized on undoped GaAs by using secondary ion mass spectroscopy and capacitance-voltage electrochemical profiling. The layer disordering with Ge is used to fabricate 5-μm-wide buried heterostructure quantum well lasers (250 μm long) with continuous wave thresholds as low as 7 mA and output powers of greater than 90 mW (both facets).

Of the various reasons to diffuse impurities into III-V semiconductors, one of the more recent is to effect impurity-induced intermixing of GaAs quantum wells (QW's) and $Al_xGa_{1-x}As$ barriers, and thus selectively increase the energy gap of a quantum well heterostructure (QWH).[1,2] For this purpose, acceptors (Zn) are much easier to use, diffusing from the vapor; donors are much less convenient to employ. To be specific, Si is an important example that, with its low vapor pressure, must be deposited on the crystal surface and then be diffused into the crystal.[3,4] Although the column VI donors possess high vapor pressures and can be used for layer intermixing, stringent control is required on the diffusion conditions to avoid chemical reaction with the crystal surface and thus surface erosion. So far, impurity-induced layer disordering (IILD) with donor (Si) diffusion has been used most effectively to fabricate high-performance buried heterostructure quantum well lasers.

In spite of the inconvenience in applying Si diffusion, high-performance single-stripe,[5,6] coupled-stripe,[7] and disordered window lasers have been fabricated. There would be an obvious advantage in achieving these results via donor diffusion from the vapor. In this letter we describe the diffusion of the Ge donor from a vapor source and utilize the process to fabricate high-performance single-stripe buried heterostructure QW lasers. Although both Ge diffusion and layer disordering from an elemental source applied to the crystal surface have been studied previously,[9,10] Ge diffusion from the vapor has not been previously reported, nor its use in device fabrication.

The Ge diffusions of interest here are carried out in sealed quartz ampoules (~ 2.5 cm^3 volume) that are evacuated to below $\sim 2\times10^{-6}$ Torr. The diffusion source consists of a 3×3 mm^2 piece of GaAs substrate onto which a layer of Ge of about 500 Å thickness has been electron-beam deposited, along with a piece of elemental As weighing ~ 15 mg. These are placed in the ampoule along with the wafer to be diffused. The anneal is performed for 10 h at temperatures of 800–820 °C. Note that at these temperatures the vapor pressure of elemental Ge is very small. However, it is known[11-13] that in the temperature range 730–750 °C the compounds GeAs and $GeAs_2$ can form in the Ga-As-Ge ternary systems. It is these compounds (and their decomposition products) that are believed to increase the Ge concentration present in the vapor phase in the annealing system, inasmuch as the vapor diffusion can be carried out by placing only elemental Ge and elemental As in the ampoule. It is not established, however, in what form the Ge exists in the vapor. The auxiliary GaAs crystal is simply used as a means to introduce a small enough amount of Ge into the annealing system so that alloy formation does not occur on the sample wafer. We have found that this vapor diffusion technique works also with an elemental Sn (+As) diffusion source at these temperatures, but attempts to diffuse Si from the vapor using this method have been unsuccessful.

Figure 1 shows the atom concentration and electron concentration in a piece of undoped bulk GaAs that has been diffused with Ge from the vapor source at a temperature of 800 °C for 10 h. The Ge concentration is measured by secondary ion mass spectroscopy (SIMS), and the electron concentration is measured using an electrochemical capacitance-voltage profiler, the Polaron PN4200. Both the shape of the SIMS profile and the large degree of electrical compensation seen in the Ge-diffused regions are reminiscent of Si diffusion, suggesting that Si and Ge may obey a similar diffusion mechanism.[14] The Ge diffusion depth is found to be relatively independent of the Ge layer thickness on the

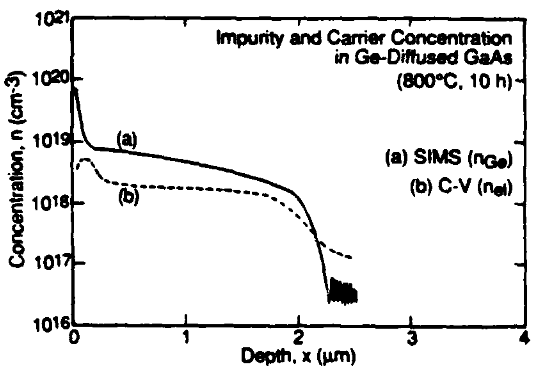

FIG. 1. Undoped bulk GaAs diffused with Ge at 800 °C (10 h) from a vapor source. (a) shows the Ge concentration as measured by SIMS. (b) shows the electron concentration measured using *C-V* electrochemical profiling in the Ge-diffused region. The Ge diffuses into the GaAs largely compensated.

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Generation of an anomalous hole trap in GaAs by As overpressure annealing

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Deep levels in high-purity n-type molecular beam epitaxy (MBE) GaAs and in undoped n-type metalorganic chemical vapor deposition (MOCVD) GaAs samples annealed with various As overpressures were investigated using constant capacitance deep level transient spectroscopy on evaporated Au Schottky barrier diodes. Anomalous hole traps, which could be measured because of a surface effect, were observed in all annealed samples. EL2 traps were created in the MBE material by the annealing, while the concentration of EL2 in the annealed MOCVD material was about the same as that before annealing. The effect of annealing on the other electron traps in these samples is also studied and reported.

Previous annealing studies on semi-insulating GaAs[1-6] have shown p-type conversion in the annealed semi-insulating material which was attributed by some to a decrease in the EL2 concentration.[4-6] Other studies have reported a high concentration of Mn at the surface of annealed layers and explained the type conversion in terms of Mn outdiffusion from the layer.[3] Studies have also been performed on annealed molecular beam epitaxy (MBE) layers which showed that EL2 was created in these samples when various caps and overpressures were used[7-9] while the concentrations of typical MBE deep traps were reduced by annealing at a sufficiently high temperature.[7,8] In the present annealing study n-type Si-doped high-purity MBE samples and an undoped metalorganic chemical vapor deposition (MOCVD) sample were used. The samples were sealed in an evacuated quartz ampoule with various amounts of solid arsenic. The ampoules were held at a temperature of 750 °C for 1 h. The arsenic overpressures were calculated assuming that all of the solid arsenic became As_4.

Figure 1 shows the carrier concentration profiles of the MBE samples annealed with the indicated arsenic overpressures. Before annealing, the MBE material had a flat carrier concentration profile with a concentration of about $3\times10^{14}/cm^3$. The annealed samples show a reduction in carrier concentration that is inversely related to the amount of arsenic overpressure. The zero bias depletion widths for the annealed samples are larger than would be expected for the corresponding carrier concentration and indicate that these samples are compensated at the surface.

Photoluminescence measurements were made on as-grown and annealed MBE samples. After annealing, the defect bound exciton lines that were present in the unannealed MBE material were no longer detectable. Another interesting effect of the annealing was a change in the dominant acceptor. Prior to annealing, the dominant acceptor in the MBE material was carbon, with a small concentration of silicon acceptors. After annealing, the concentration of silicon acceptors was increased so that silicon acceptors became dominant. This change indicates that the intentional silicon dopant atoms are switching from Ga sites to As sites, contrary to what might be expected with an arsenic overpressure during the annealing. However, the data in Fig. 1 show that higher As overpressures seem to inhibit this site switching. A full photoluminescence study of the annealing effects on the acceptor concentrations is planned.

Constant capacitance-deep level transient spectroscopy (CC-DLTS) measurements were performed on all of the annealed samples using an apparatus that has been described previously.[10] Gold Schottky barrier diodes and nickel-tin ohmic contacts were formed on the samples. Devices fabricated on annealed material have lower reverse-bias breakdown voltages than those fabricated on unannealed material. However, all of the devices had quality factors greater than 10, indicating that series resistance was not a factor in the DLTS measurements. All spectra were taken by pulsing the diodes between a reverse bias of approximately 2 V and zero bias. Representative spectra of the as-grown and annealed MBE samples are shown in Fig. 2(a). The spectrum of the as-grown MBE material contains the electron traps M1, M3, and M4 that are typical of MBE material. M3 is the dominant trap with a trap concentration of $4\times10^{12}/cm^3$. After annealing, the dominant feature of the spectrum is a hole trap labeled NP1. The energy level for NP1 is 0.67 eV above the valence band and the trap has a capture cross section of $1\times10^{-13} cm^2$. Other effects of annealing are a reduction of the concentration of M3 by a factor of 4 and the

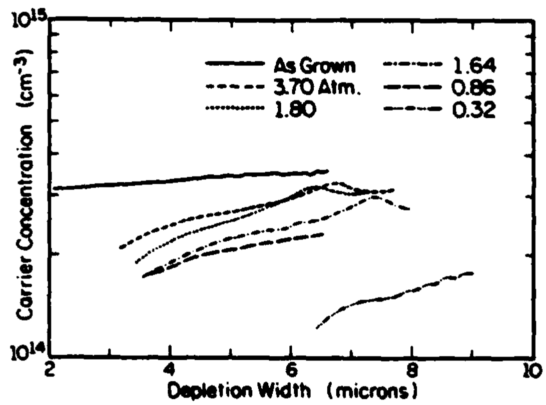

FIG. 1. Carrier concentration profile of a MBE sample before and after annealing with various arsenic overpressures.

IMPURITY-INDUCED LAYER DISORDERING IN $Al_xGa_{1-x}As$-GaAs QUANTUM WELL HETEROSTRUCTURES

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ABSTRACT

Selective interdiffusion of Al and Ga at $Al_xGa_{1-x}As$-GaAs heterointerfaces can be carried out by conventional masking procedures and diffusion of acceptor impurities (e.g., Zn), or donor impurities (e.g., Si), or also by ion implantation. This process, impurity-induced layer disordering (IILD), makes it possible to convert quantum well heterostructures (QWHs) such as $Al_xGa_{1-x}As$-GaAs superlattices (SLs) into bulk homogeneous $Al_yGa_{1-y}As$ where y is the average Al composition of the QWH or SL. Since the IILD process is maskable and thus selective, heterojunctions can be formed in directions perpendicular to the crystal growth direction, i.e., between as-grown "ordered" and IILD "disordered" regions. To date this process has been used most effectively in the fabrication of buried-heterostructure QW lasers, single and multiple stripe, where the disordered regions provide both optical and electrical confinement. The IILD process has also been used to advantage in the fabrication of high power laser diodes with non-absorbing "windows" at the laser facets and thus with better immunity from facet damage.

In this paper we present data on the application of the IILD process to the fabrication of buried-heterostructure QW laser diodes. We also describe possible mechanisms by which the impurity-induced layer disordering proceeds based on Column III "Frenkel" defects and the influence of the crystal Fermi level on the defect solubility. These mechanisms are supported by experimental data.

INTRODUCTION

Impurity-induced layer disordering (IILD) was discovered in 1980 by Laidig, et al. [1] while attempting to convert, via Zn diffusion for phonon experiments [2], undoped $Al_xGa_{1-x}As$-GaAs superlattices (SLs) to p-type material. It was quickly recognized [3] that the layer intermixing of the $Al_xGa_{1-x}As$-GaAs SL that accompanies the relatively low temperature Zn diffusion provides a convenient means of converting lower energy gap thin layer heterostructures into higher gap homogeneous bulk-crystal alloy. The selectivity of the diffusion process, which can be masked, then allows the fabrication of heterojunctions normal to the crystal growth direction and thus normal to the layers (and doping) that are part of the epitaxial crystal growth. The IILD occurs because of the Zn impurity's ability to increase the Column III (Al and Ga) atom self-diffusion rates many orders of magnitude over that of ordinary thermal Al-Ga interdiffusion. Since the initial discovery of IILD via Zn diffusion [1], many different atomic species have been found to promote IILD, either through impurity diffusion, ion implantation and subsequent crystal annealing, or incorporation during crystal growth and then subsequent annealing. For example, besides the acceptor Zn, the acceptors Be [4] and Mg [5] are known to promote IILD, and

HYDROGENATION OF GaAs AND APPLICATION TO DEVICE PROCESSING

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ABSTRACT

Exposure of GaAs and AlGaAs to a hydrogen plasma has been shown to result in a significant change in the electrical and optical properties. The changes are related to the electrical deactivation of the deep and shallow impurities by hydrogenation. Spectroscopic and electrical measurements have shown that Si donors and C acceptors in high purity GaAs can be passivated by hydrogenation. Hydrogenation of p-type GaAs and AlGaAs has resulted in highly resistive material. SiO_2 was found to be a suitable mask for the hydrogenation process. Single and multiple stripe geometry lasers have been fabricated by properly masking the laser structure. The lasers produced using the hydrogenation process have low threshold currents and are capable of cw room temperature operation.

INTRODUCTION

Recent studies of hydrogenation have resulted in a better understanding of the passivation of deep and shallow impurities and hydrogenation kinetics [1-9]. The electrical and optical properties of GaAs can be changed significantly after exposure to a hydrogen plasma. There have been many reports on the neutralization of shallow donors in implanted and heavily doped GaAs [6-8]. The results on the neutralization of shallow acceptors have been reported [6,9], but the results have not been very consistent. Recent results on the passivation of AlGaAs [6,10] have shown similar behavior to those on GaAs. These results offer the possibility of using hydrogenation as a processing technique. Hydrogenation has been used to realize isolation regions in a stripe geometry laser [11].

In this paper, the properties of high purity material before and after hydrogenation will be summarized. The characterization techniques include photothermal ionization spectroscopy (PTIS), low temperature photoluminescence (PL), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), capacitance voltage (C-V) and Hall effect measurements. The effects of hydrogenation on AlGaAs and GaAs-on-Si samples will be discussed. In addition, the results of the use of hydrogenation to realize isolation regions in single and multiple stripe quantum well lasers will be presented.

EXPERIMENT

The plasma reactor, hydrogenation conditions, details of the characterization techniques, and sample preparation used in the high purity

Ref. 9

Short-wavelength (~625 nm) room-temperature continuous laser operation of $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ quantum well heterostructures

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Data are presented demonstrating very-short-wavelength (625 nm) room-temperature (300 K) continuous (cw) photopumped laser operation of $In_{1-y}(Al_xGa_{1-x})_yP$-$In_{1-y}(Al_{x'}Ga_{1-x'})_yP$ quantum well heterostructures grown lattice matched ($y \approx 0.5$) on a GaAs substrate via metalorganic chemical vapor deposition. In addition, 300 K pulsed laser operation ($J_{th} \sim 10^4$ A/cm^2, 625 nm) of diodes fabricated from the same crystal is described.

Because of the high-energy gap at the direct-indirect crossover of $In_{1-x}Ga_xP$ ($x \equiv x_c \approx 0.73$, $E_\Gamma = E_X \approx 2.24$ eV)[1,2] and the long-known fact, beginning with $Al_xGa_{1-x}As$ studies,[3,4] that Al can be substituted for Ga with only slight lattice change in a III-V crystal, it has long been appreciated that the substitution of Al for Ga in $In_{1-x}Ga_xP$ can serve as the basis for even higher gap and thus shorter wavelength light-emitting diodes and lasers. The shift of $In_{1-x}Ga_xP$ to $In_{1-y}(Al_xGa_{1-x})_yP$ ($0<x<1$, $0<y<1$), which has been made practical by the development of metalorganic chemical vapor deposition (MOCVD) or MO vapor phase epitaxy (MOVPE),[5,6] makes possible the fabrication of high-gap $In_{1-y}(Al_{x'}Ga_{1-x'})_yP$-$In_{1-y}(Al_xGa_{1-x})_yP$ heterojunctions and quantum well heterostructures (QWH's). The most important case recently receiving attention is that of the $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ alloy ($y \approx 0.5$),[1,2] which is (as is $In_{0.5}Ga_{0.5}P$) lattice matched to GaAs and yields shorter wavelength lasers than the $Al_xGa_{1-x}As$ system.[7-12] Unlike (AlGa)As, however, (InAlGa)P is not intrinsically lattice matched to GaAs; it is not a simple matter to keep the composition y fixed ($y \approx 0.5$), and keep strain and defects out of $In_{0.5}(Al_xGa_{1-x})_{0.5}$ QWH's grown on GaAs substrates. Hence, for various reasons pertaining to crystal quality and as yet uncertain energy band properties, it is not known what the shorter wavelength limits might be for this system for use as a room-temperature (300 K) continuous (cw) laser. In the present letter we demonstrate, on photopumped $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ QWH samples, cw 300 K stimulated emission to wavelengths as short as 625 nm. Pulsed diode laser operation (300 K) at the same wavelength occurs at $J \sim 10^4$ A/cm^2.

The epitaxial $In_{1-y}(Al_xGa_{1-x})_yP$ layers are grown lattice matched ($y \approx 0.5$) on an n-type (100) GaAs substrate with the use of a horizontal MOCVD (MOVPE) reactor.[11] Trimethylaluminun (TMAl), trimethylgallium (TMGa), trimethylindium (TMIn), and PH_3 are used as the sources for the primary crystal components Al, Ga, In, and P, respectively. Hydrogen selenide and dimethylzinc are used as n- and p-type dopant sources. Figure 1 shows a scanning electron microscope (SEM) image (cross section) of the active region of the p-n doped $In_{0.5}(Al_xGa_{1-x})_{0.5}P$-$In_{0.5}(Al_{x'}Ga_{1-x'})_{0.5}P$ QWH laser crystal of interest. The quantum well active region consists of (1) a 1.0 μm n-type lower confining layer ($x = 0.8$), (2) an undoped 0.2 μm symmetric waveguide region ($x = 0.65$) with a 200 Å quantum well ($x = 0.2$) at its center, (3) a 1.0 μm p-type upper confining layer ($x = 1$), and (4) a 0.5 μm p-type GaAs contact layer. The crystal surface exhibits a fine crosshatched pattern (not shown), which indicates that this crystal is not completely lattice matched. This is a known sign of strain and defects.[13,14] As a consequence of strain and defects, the QWH crystal of Fig. 1 exhibits higher laser threshold than desired (Figs. 2 and 3) and relatively poor cw 300 K operating lifetime (photopumped sample of Fig. 3).[14,15]

Figure 2 shows the spectral behavior of an oxide stripe laser (20×400 μm^2) fabricated on the $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ QWH of Fig. 1. The oxide stripe laser diodes[16] are fabricated by first depositing 1000 Å of SiO_2 on the p-type side of the wafer (via chemical vapor deposition) and by then defining 20-μm-wide stripe openings. After a shallow Zn diffusion step (~1000 Å), the wafer is thinned to 100 μm, and contacted with Cr-Au (evaporated) on the p side and Ge-Au (evaporated and alloyed) on the n side. The wafer is cleaved to give cavity lengths of ~400 μm. The finished diode of Fig. 2 is pulse excited (100 ns, 300 K). At 500 mA (6×10^3 A/cm^2) the spontaneous emission peak occurs at 633 nm [1.96 eV, curve (a)]. Band filling occurs at higher current, and at 900 mA [10^4A/cm^2, curve (b)] spec-

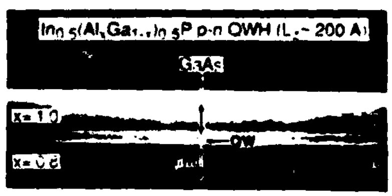

FIG. 1. Scanning electron microscope (SEM) image showing in cross section the active region of a p-n $In_{1-y}(Al_xGa_{1-x})_yP$-$In_{1-y}(Al_{x'}Ga_{1-x'})_yP$ quantum well heterostructure (QWH) grown latticed matched on GaAs with the use of metalorganic chemical vapor deposition (MOCVD). The layer compositions (x) are indicated along the left edge.

[a] Kodak fellow.
[b] Shell fellow.

Impurity-induced layer disordering of high gap $In_y(Al_xGa_{1-x})_{1-y}P$ heterostructures

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Data are presented showing the impurity-induced layer disordering (IILD), via low-temperature (600–675 °C) Zn diffusion, of $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ quantum well heterostructures and an $In_{0.5}Al_{0.2}Ga_{0.3}P$-GaAs heterojunction grown using metalorganic chemical vapor deposition. Secondary ion mass spectroscopy, transmission electron microscopy, and photoluminescence are used to confirm IILD, which occurs via atom intermixing on the column III site aided by column-III-atom interstitials. In addition, high-temperature anneals (800–850 °C) are performed on the same crystals to confirm the thermal stability of the heterointerfaces.

The $In_y(Al_xGa_{1-x})_{1-y}P$ alloy lattice matched to GaAs ($y \simeq 0.5$) is an important light-emitting system since it allows laser operation at a shorter wavelength than the AlGaAs-GaAs system. Continuous (cw) room-temperature (300 K) laser diode operation has already been achieved at wavelengths ~6800 Å,[1,2] as well as cw 300 K photopumped laser operation of quantum well heterostructures (QWH's) at 6250 Å.[3] Of the different types of stripe laser structures possible in (InAlGa)P, the buried heterostructure is most desirable since the built-in optical waveguide can result in stable radiation patterns, and both carrier and optical confinement give the potential for low threshold currents. Impurity-induced layer disordering (IILD),[4-8] with its Al-Ga interdiffusion and energy-gap increase, has proven to be an effective process for the fabrication of low threshold $Al_xGa_{1-x}As$-GaAs QWH buried heterostructure laser diodes. The fact that IILD promotes Al-Ga interdiffusion at AlGaAs-GaAs heterobarriers suggests that the same mechanism will be effective in (InAlGa)P, which has not been previously established and is the subject of this paper. We report data on the impurity-induced layer disordering, via Zn diffusion, of $In_{0.5}(Al_{x'}Ga_{1-x'})_{0.5}P$-$In_{0.5}(Al_xGa_{1-x})_{0.5}P$ QWH's and also an $In_{0.5}(Al_{0.4}Ga_{0.6})_{0.5}P$-GaAs heterojunction. For Zn diffusion temperatures ~600 °C, the layer disordering occurs on the column III site and, consistent with other data,[9-12] can be accounted for by a mechanism involving column III interstitials.

The crystals used in this study are undoped and are grown using metalorganic chemical vapor deposition (MOCVD).[13] The growth takes place in a horizontal reactor using sources of trimethylaluminum, trimethylgallium, trimethylindium, PH_3, and AsH_3. The IILD Zn diffusions (600–675 °C) are carried out in sealed ampoules with diffusion sources of either $ZnAs_2$ or elemental Zn and P, with little difference in the IILD results. Besides IILD with lower temperature Zn diffusion, higher temperature anneals also have been performed at 815–850 °C with only a phosphorus overpressure to investigate the thermal stability of the heterostructures.

The samples have been analyzed using secondary ion mass spectroscopy (SIMS), transmission electron microscopy (TEM), and photoluminescence. Wafers are prepared for photoluminescence and laser operation (77 K) by removing the GaAs substrate and any GaAs cap layers or buffer layers, and then thinning the remaining epitaxial layers sufficiently to give a 1–2 μm sample thickness. Cleaved samples are heat sunk in In under a sapphire window and excited with an Ar^+ laser (5145 Å).

Figure 1(a) shows SIMS profiles of Al and Ga concentration versus depth for an as-grown $In_{0.5}(Al_{x'}Ga_{1-x'})_{0.5}P$-$In_{0.5}(Al_xGa_{1-x})_{0.5}P$ QWH. The structure consists of $In_{0.5}(Al_{0.9}Ga_{0.1})_{0.5}P$ confining layers with an $In_{0.5}(Al_{0.7}Ga_{0.3})_{0.5}P$ waveguide region of ~0.2 μm thickness, and a single $In_{0.5}(Al_{0.1}Ga_{0.9})_{0.5}P$ QW (at 0.6 μm) of thickness ~200 Å at the waveguide center. The lasing wave-

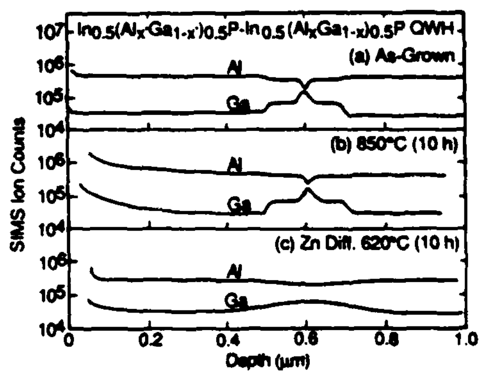

FIG. 1. SIMS profiles of the Al and Ga concentrations of an $In_{0.5}(Al_{0.7}Ga_{0.3})_{0.5}P$-$In_{0.5}(Al_{0.1}Ga_{0.9})_{0.5}P$ QWH [the confining layers are $In_{0.5}(Al_{0.9}Ga_{0.1})_{0.5}P$] for (a) the as-grown crystal, (b) after thermal annealing (850 °C, 10 h), and (c) after Zn diffusion at 620 °C (10 h). The QWH remains intact for the high-temperature anneal (b) but is unstable against the much lower temperature Zn diffusion (c).

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Dislocation reduction by impurity diffusion in epitaxial GaAs grown on Si

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Data are presented showing that low-temperature Zn diffusion (680 °C) is effective in reducing the dislocation density in epitaxial GaAs grown on Si. The GaAs-on-Si is analyzed using both cross-sectional and plan-view transmission electron microscopy. For comparison, simple thermal annealing of the GaAs-on-Si at higher temperature (850 °C) is also performed and analyzed. The reduction in the dislocation density that occurs with Zn diffusion is suggested to be due to the increased concentration of point defects generated during the Zn diffusion, resulting in enhanced dislocation climb. This mechanism is consistent with impurity-induced layer disordering, via Zn diffusion, in $Al_xGa_{1-x}As$-GaAs heterostructures.

If GaAs grown epitaxially on Si is to become more than just of research interest, and is to realize its potential as a sturdier GaAs "substrate" or a combined GaAs optoelectronic-Si electronic material, then the high defect (dislocation) density in the epitaxial GaAs caused by the 4% GaAs-Si lattice mismatch must be reduced. The nature of this problem has been discussed elsewhere,[1] as well as various attempts to reduce the defect density by relatively high-temperature annealing procedures.[1-3] Thermal annealing is to some extent an effective procedure for reducing defects in GaAs-on-Si but of itself may not be sufficient. Also, in many cases higher temperature annealing may not be desired. In any case, other methods to reduce the defects in GaAs-on-Si are needed. In this letter we describe impurity diffusion (Zn) into GaAs-on-Si at lower temperatures (680 °C) that is effective in removing defects (dislocations). The possibility is discussed that the point defects generated during the Zn diffusion and the mechanisms responsible for impurity-induced layer disordering in $Al_xGa_{1-x}As$-GaAs heterostructures play a role.

The samples used in this study consist of ~2-μm-thick GaAs epitaxial layers grown, by molecular beam epitaxy (MBE), on Si substrates tilted 3° from [100] orientation toward the [011]. The MBE crystal growth has been described previously.[1] Briefly, a nucleation layer of GaAs ~500 Å thick is grown at a temperature of 500 °C. The growth temperature is then ramped to 575 °C and held constant for the remaining GaAs crystal growth. The resultant layer has a smooth, featureless surface morphology. Although it is widely appreciated that for GaAs grown on Si the crystal quality improves (less dislocations) in the GaAs material further from the GaAs-Si interface, the relatively thin epitaxial layers used here (~2 μm) are grown basically to serve as a buffer layer for the subsequent growth of an $Al_xGa_{1-x}As$-GaAs laser structure.[4]

Zinc diffusion using a $ZnAs_2$ source is performed into GaAs-on-Si in a sealed quartz ampoule at a temperature of 680 °C (6 h), or even lower. Further thermal annealing with simply an excess As overpressure has also been performed on both Zn-diffused wafers (850 °C, 0.5 h) and, for comparison, on as-grown (undiffused) wafers (850 °C, 0.5 h and 680 °C, 6 h). The GaAs-on-Si material has been analyzed using transmission electron microscopy (TEM). Figure 1 shows TEM cross sections of (a) the as-grown GaAs-on-Si, (b) a sample after thermal annealing at 680 °C (6 h), and (c) another sample after Zn diffusion at 680 °C (6 h). The cross sections show that even a simple thermal anneal at 680 °C, Fig. 1(b), is to some extent effective in reducing the dislocation density in GaAs-on-Si. However, Zn diffusion for the same time and temperature, Fig. 1(c), is much more effective than a simple thermal anneal. Zinc diffusion [Fig. 1(c)] results in a greatly reduced dislocation density compared to the as-grown epitaxial GaAs-on-Si, Fig. 1(a), and compared also to the simple thermal anneal, Fig. 1(b). In analyzing GaAs grown on Si substrates misorientated from [100] toward [011], we see significant differences in defect densities when viewing the sample in perpendicular ⟨110⟩ directions, e.g., directions either parallel or perpendicular to the substrate tilt direction.[5] Both directions have been analyzed, with Fig. 1 showing in each case the highest dislocation densities. The largest difference in defect density for the two different directions is found for the as-grown wafer, Fig. 1(a), while for the Zn-diffused GaAs-on-Si, Fig. 1(c), little difference in defect densities is found for the two perpendicular directions.

Figure 2 shows TEM cross sections of the same GaAs-on-Si wafer after (a) a thermal anneal at 850 °C (0.5 h), (b) the Zn diffusion [Fig. 1(c)] at 680 °C (6 h), and (c) an 850 °C (0.5 h) thermal anneal of a wafer which has been first Zn diffused at 680 °C (6 h). Note that the low-temperature Zn diffusion (680 °C), Fig. 2(b), is more effective in removing dislocations than the significantly higher temperature anneal at 850 °C shown in Fig. 2(a). The 850 °C (0.5 h) anneal of the Zn-diffused GaAs-on-Si shows a further reduction in dislocations at the GaAs-Si interface. Cracking of the 2-μm-thick Zn-diffused GaAs epitaxial layer is also found

Ref. 12

Impurity diffusion and layer interdiffusion in $Al_xGa_{1-x}As$-GaAs heterostructures

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Data are presented and a model describing the diffusion of the donor Si in GaAs from grown-in dopant sources. In addition, the effects of background impurities on Si diffusion and layer interdiffusion in $Al_xGa_{1-x}As$-GaAs superlattices are described. These results are obtained on epitaxial GaAs samples with alternating doped and undoped layers and on $Al_xGa_{1-x}As$-GaAs superlattices with doped (Si or Mg) layers. The layer-doped GaAs and the $Al_xGa_{1-x}As$-GaAs superlattices have been grown using metalorganic chemical vapor deposition and are characterized using secondary ion mass spectroscopy and transmission electron microscopy. Different annealing conditions are used to study the interaction between the grown-in impurities and the native defects of the crystal controlling the diffusion processes. The model describing the impurity diffusion and layer (Al-Ga) interdiffusion is based on the behavior of column III vacancies, V_{III}, and column III interstitials, I_{III}, and the control of their concentration by the position of the crystal Fermi level and the crystal stoichiometry. Experimental data show that *n*-type $Al_xGa_{1-x}As$-GaAs superlattices undergo enhanced layer interdiffusion because of increased solubility of the V_{III} defect, while enhanced layer interdiffusion in *p*-type superlattices is caused by an enhanced solubility of I_{III}. The model employed is consistent with the experimental data and with the data of previous work.

I. INTRODUCTION

The $Al_xGa_{1-x}As$-GaAs crystal system is important for use in a large range of lattice-matched heterostructure devices. Because of the good lattice match between AlAs and GaAs, it is possible to grow readily thin layered structures, including quantum-well heterostructures (QWHs), across the whole range of $Al_xGa_{1-x}As$ alloy compositions. The study of impurity diffusion (dopants) in this alloy system is important not only because semiconductor devices are usually based around critically placed *p-n* junctions, but also because it has been found that the diffusion of impurities through $Al_xGa_{1-x}As$-GaAs heterojunctions can influence the self-diffusion rate (interdiffusion rate) of Al and Ga atoms across heterobarriers.[1,2] The modern capability to grow thin layered structures, along with now the knowledge that impurities promote interdiffusion of primary crystal components, makes it possible to study the self-diffusion of the column III atoms in III-V crystals ($Al_xGa_{1-x}As$). This gives added insight into the nature of the important defects governing both impurity diffusion and self-diffusion in III-V crystals.

In this paper we present newer data on the diffusion of the donor Si in GaAs from grown-in impurity sources (layered sources) and show that these data are consistent with previous studies of Si diffusion from external sources, e.g., Si deposited on the crystal surface.[3-7] We also present data on the effect of grown-in impurities (Mg or Si) on layer interdiffusion in $Al_xGa_{1-x}As$-GaAs superlattices (SLs),[8] along with a model of how impurity (dopant) atoms and crystal annealing conditions can influence the column III atomic self-diffusion rates. These ideas are shown to be consistent with previous experimental data on both impurity diffusion and layer interdiffusion (layer intermixing) in $Al_xGa_{1-x}As$-GaAs quantum-well heterostructures (QWHs).

II. EXPERIMENTAL PROCEDURE

The crystals used in this work have been grown in an EMCORE GS-3000 reactor using metalorganic chemical vapor deposition (MOCVD).[9] First, we investigate the effects of the annealing environment on the diffusion of Si from localized grown-in sources (layered sources) in GaAs. Two crystals are examined that are grown at 650 °C on ⟨100⟩ GaAs substrates. Four Si-doped layers of thickness ~1000 Å each separated by ~3000 Å of undoped GaAs are incorporated in the two crystals. In the doped regions the SiH_4 dopant flow is adjusted to give an electron concentration of $n_e \sim 4\times10^{18}$ cm^{-3} in the first wafer and $n_e \sim 1.7\times10^{18}$ cm^{-3} in the second. These concentrations are determined with a POLARON PN 4200 capacitance-voltage (*C-V*) electrochemical profiler. Both the as-grown and the thermally annealed crystals (diffused wafers) are analyzed using secondary ion mass spectroscopy (SIMS). The atomic Si concentration (n_{Si}) measured by SIMS is found to follow closely the change in electron concentration measured by *C-V* profiling, showing that most of the atomic Si is incorporated as donors.

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 0021-8979/88/161838-07$02.40

Effects of microcracking on $Al_xGa_{1-x}As$-GaAs quantum well lasers grown on Si

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Data are presented demonstrating continuous (cw) 300 K operation of *p-n* $Al_xGa_{1-x}As$-GaAs quantum well heterostructure lasers grown on Si and fabricated with naturally occurring microcracks running parallel to or perpendicular to the laser stripe. Operation for over 17 h is demonstrated for a diode with a parallel microcrack inside the active region. Diodes with microcracks perpendicular to the laser stripe exhibit relatively "square" light output versus current (*L-I*) characteristics and spectral behavior indicating internal reflections involving coupled multiple (internal) cavities. The lasers have operated (cw, 300 K) as long as 16 h.

Since the earlier successful fabrication of III-V semiconductor lasers grown on Si substrates,[1,2] there has been continued interest in improving the performance of these devices beyond simply pulsed 300 K operation.[3,4] We have recently achieved continuous-wave (cw) room-temperature operation of $Al_xGa_{1-x}As$-GaAs lasers grown on Si, initially in photopumped operation[5,6] and also as *p-n* laser diodes.[7,8] To date, $Al_xGa_{1-x}As$-GaAs laser diodes grown on Si have been operated cw room-temperature for over 10 h.[9] Other workers have also reported cw room-temperature operation of $Al_xGa_{1-x}As$-GaAs lasers grown on Si but apparently not for times beyond 4 min.[10,11] Clearly major problems face the GaAs-Si system: $Al_xGa_{1-x}As$-GaAs lasers grown on Si are mismatched 4% in lattice size relative to Si and exhibit a ~250% difference in thermal expansion. At the III-V crystal growth temperature the large lattice mismatch relative to Si is accommodated by a high density of dislocations. When the system is cooled to room temperature, the large difference in thermal expansion results in highly strained epitaxial III-V layers. Although the III-V epitaxial crystal quality, measured in terms of dislocation density, improves further from the GaAs-Si interface, the strain in the epitaxial layers increases as the layer thickness increases. Above a certain thickness microcracks form in the epitaxial layer and to some extent relieve the strain. It is the effect of these microcracks on the performance of the laser diodes grown on Si that is at issue in this letter. We show that the microcracking occurring in $Al_xGa_{1-x}As$-GaAs lasers grown on Si can have a dominant effect on the spectral characteristics of these devices. Also, the microcracking is shown to have no particularly deleterious effect on the laser devices in terms of threshold or operating lifetime and, in fact, may offer some benefit by providing strain relief.

The crystal growth and device fabrication used in this study have been described previously[5-8] and will be reviewed only briefly. First a 2 μm GaAs *n*-type ($n_{Si} \sim 10^{18}$ cm^{-3}) buffer layer is grown directly on the n^+-Si substrate using molecular beam epitaxy (MBE). The wafer is then transferred to a metalorganic chemical vapor deposition (MOCVD) growth system in which an $Al_xGa_{1-x}As$-GaAs *p-n* single quantum well (QW) separate confinement laser structure is grown. The total thickness of the III-V epitaxial layers (MBE + MOCVD) is ~5 μm. Laser diodes are fabricated by defining 10-μm-wide oxide stripe openings to contact the *p* side (epitaxial layer side). The *p*-side metallization consists of 250 Å of Cr followed by 1000 Å of Au. The *n* side is contacted, via the n^+-Si substrate, using a 500 Å alloyed Al metallization on the Si followed by 250 Å of Cr and 1000 Å of Au. Typical pulsed thresholds of these devices are 90–110 mA for 350-μm-long cavities. For cw operation the laser diodes are mounted on a copper block either in a "junction-up" or "junction-down" configuration. It has been shown that cw operation in the "junction-up" configuration is aided in part by the higher thermal conductivity of the Si substrate.[9]

We have previously found that when the total III-V epitaxial layer thickness is ~10 μm, cracking and severe warping occur in the epitaxial layers.[5] For a total thickness of ~5 μm only a few microcracks are observed in the top-surface III-V epitaxial layer after crystal growth. However, when the wafer is cleaved into smaller pieces to process into laser diodes, the flexing of the Si substrate together with the built-in strain in the epitaxial material can introduce a high density of microcracks in the final III-V laser structure. These microcracks run in the ⟨110⟩ directions and are typically spaced ~20–500 μm apart in areas of the crystal in which the microcracks are densest. Therefore, there is a significant probability for some of these microcracks to be either parallel to the laser stripe (near or even within it), or be perpendicular to the laser stripe. For example, Fig. 1 shows a photograph of a microcrack running along the inside of an oxide stripe opening, and thus *in* the laser active region. The quantum well heterostructure laser of Fig. 1 is shown after metallization, and, even through the 250 Å of Cr and 1000 Å of

Ref. 14

Thermal behavior and stability of room-temperature continuous $Al_xGa_{1-x}As$-GaAs quantum well heterostructure lasers grown on Si

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Data are presented on the thermal characteristics of *p-n* $Al_xGa_{1-x}As$-GaAs quantum well heterostructure (QWH) diode lasers grown on Si substrates. Continuous 300-K operation for over 10 h is demonstrated for lasers mounted with the junction side away from the heat sink ("junction-up") and the heat dissipated through the Si substrate. "Junction-up" diodes that are grown on Si substrates have measured thermal impedances that are 38% lower than those grown on GaAs substrates, with further reductions possible. Thermal impedance data on "junction-down" diodes are presented for comparison. Measured values are consistent with calculated values for these structures. Low sensitivity of the lasing threshold current to temperature is also observed, as is typical for QWH lasers, with T_0 values as high as 338 °C.

I. INTRODUCTION

The growth of III-V semiconductors on Si is currently receiving much attention because Si substrates are cheaper, sturdier, and have better thermal properties than III-V semiconductor substrates and because III-V devices are capable of light emission and higher speed. Now III-V semiconductor devices potentially can be merged with more highly developed Si integrated circuit technology. Despite the large crystal lattice mismatch (4%) and the difference in the thermal expansion coefficients of GaAs and Si, which result in high defect densities in the epitaxial GaAs, recent progress in the study of $Al_xGa_{1-x}As$-GaAs heterostructures and quantum well heterostructures (QWHs) grown on Si substrates indicates considerable promise for this hybrid technology.

Device-quality GaAs must have reasonably low defect densities, particularly for injection devices, as it has been shown that the formation and propagation of dislocation networks depends primarily upon carrier recombination rather than upon current flow.[1] Perhaps the most demanding test of the GaAs-on-Si material is that of continous (cw) 300-K laser operation of a III-V QWH grown on a GaAs-on-Si substrate. Continuous 300-K laser operation, the most severe test, was first achieved (though not reliably) for a photopumped multiple well $Al_xGa_{1-x}As$-GaAs quantum well heterostructure laser grown on GaAs-on-Si.[2] By simplifying the structure to a single GaAs quantum well, Nam *et al.* reduced the number of active region interfaces threaded by dislocations, thus making lower threshold and more reliable (cw, 300 K) photopumped laser operation possible.[3] By utilizing such a single-well structure with *p* and *n* doping, Deppe *et al.* (spring, 1987) realized the first room-temperature cw *p-n* diode $Al_xGa_{1-x}As$-GaAs QWH lasers grown on GaAs-on-Si.[4,5] Operation for over 4 h has been demonstrated.[6] Another laboratory later reported presumably cw room-temperature operation[7]; a further report indicated ~5-min operation.[8] These developments, along with earlier reports of pulsed laser operation,[9–12] suggest that practical high level $Al_xGa_{1-x}As$-GaAs diodes grown on Si substrates can indeed be realized.

In the present work we describe further progress in the cw 300-K operation of $Al_xGa_{1-x}As$-GaAs QWH lasers grown on Si, including the important demonstration that cw 300-K laser operation is possible with the diode heat sunk from the side of the Si substrate ("junction-up") and *not* with the III-V semiconductor active layers mounted, as usual, downward on the heat sink ("junction-down"). In the "junction-up" configuration over 10 h of cw 300-K laser operation is demonstrated. This is potentially very important if III-V optoelectronics is to be successfully integrated with Si technology, where integrated circuit (IC) style processing may necessitate that most lasers fabricated on an integrated optoelectronic "chip" will have the junction region (the active region) turned upward and not downward on a heat sink. This increases the importance of the issue of thermal impedance, which is a measure of how well the heat generated in a laser diode is dissipated. The stability of the laser diodes of the present work, and of Refs. 5 and 6, makes it possible to perform more extensive characterization measurements on these diodes. In this paper the thermal characteristics of these diodes are examined. Measurements and calculations of thermal impedance are presented for GaAs-on-Si and GaAs-on-GaAs lasers mounted both junction-up and, for comparison, junction-down. We show that the thermal impedance of junction-up lasers is reduced by the higher conductivity Si substrates. Also presented are measurements showing the temperature sensitivity of the lasing threshold current for the QWH GaAs-on-Si diodes.

Ref. 15

Short-wavelength ($\lesssim$6400 Å) room-temperature continuous operation of *p-n* $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ quantum well lasers

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Data are presented demonstrating short-wavelength ($\lesssim$6400 Å) continuous (cw) laser operation of *p-n* diode $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ multiple quantum well heterostructure (QWH) lasers grown lattice matched on GaAs substrates using metalorganic chemical vapor deposition. In the range from -30 °C to room temperature (RT$\approx$300 K, $\lambda \approx 6395$ Å) the threshold current density changes from 2.3×10^3 A/cm² (-30 °C) to 3.7×10^3 A/cm² (RT, 300 K). The cw 300 K photopumped laser operation of the same quaternary QWH crystal is an order of magnitude lower in threshold (7×10^3 W/cm², $J_{eq} \sim 2.9\times10^3$ A/cm²) than previously reported for this crystal system, and agrees with the successful demonstration of cw 300 K laser diodes at this short wavelength.

Since the time of the first semiconductor lasers (1962),[1] an important goal has been to achieve continuous (cw) room-temperature (300 K) operation, not only at longer wavelengths, but also at shorter wavelengths (visible wavelengths).[2] In ternary III-V semiconductors the shortest wavelength stimulated emission occurs in the $In_{1-y}Ga_yP$ system.[3,4] Aluminum substitution for Ga in this system (as is known from $Al_xGa_{1-x}As$)[5,6] leads, without lattice change, to the higher gap quaternary $In_{1-y}(Al_xGa_{1-x})_yP$[7] and thus, by varying x, to the possibility of higher gap heterostructures. Of further importance, the development of metalorganic chemical vapor deposition (MOCVD)[8] makes possible both Al substitution in $In_{1-y}Ga_yP$ and the construction of $In_{1-y}(Al_xGa_{1-x})_yP$ quantum well heterostructures (QWH's), including, above all, the practical case of the quaternary layers lattice matched ($y \approx 0.5$) on a GaAs substrate. A major problem is how to accomplish this without variation in the composition y ($y \approx 0.5$) between layers (i.e., without strain generation), and at composition values x giving higher energy gaps (>1.91 eV). A number of workers[9-14] have reported some degree of success in constructing visible spectrum $In_{1-y}(Al_xGa_{1-x})_yP$ heterostructure lasers. Recently we have shown for the simpler case of "super" heat sunk photopumped $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ QWH's that cw 300 K laser operation is possible at wavelengths as short as 6250 Å,[15] unfortunately, however, at thresholds an order of magnitude too high for cw 300 K laser diode operation. In the present letter we show that $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ QWH's can be improved sufficiently to give cw 300 K diode laser operation at wavelengths $\lesssim$6400 Å, or near that of the He-Ne laser.

The epitaxial layers for these laser structures are grown on (100) *n*-type GaAs substrates by metalorganic chemical vapor deposition (MOCVD) in a horizontal reactor. Sources for the constituents of the various $In_{1-y}(Al_xGa_{1-x})_yP$ layers are trimethylindium, trimethylgallium, trimethylaluminum, and phosphine (PH_3). Zn for *p*-type doping and Te for *n*-type doping are provided by dimethylzinc and diethyltelluride, respectively. Figure 1 shows schematically the layer structure in the active region of the crystals used in these experiments. Carrier and optical confinement are provided by a 1.0 μm *p*-type $In_{0.5}(Al_{0.9}Ga_{0.1})_{0.5}P$ upper and an *n*-type lower confining layer. The crystal composition is linearly graded towards the active region, which, in its center, consists of four $In_{0.5}(Al_{0.2}Ga_{0.8})_{0.5}P$ quantum wells of 200 Å (L_z) thickness separated by three 100 Å (L_B) $In_{0.5}(Al_{0.5}Ga_{0.5})_{0.5}P$ barriers. The upper confining layer is capped by a heavily Zn-doped contact layer.

Before stripe geometry diodes are assembled on these crystals, the bottom substrate and intermediate buffer layers are removed, as well as the top contact layer, and the QWH crystal is evaluated by photopumping. The crystal is prepared for photopumping by first removing the contact layer

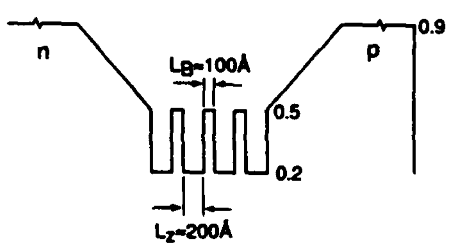

FIG. 1. Schematic diagram showing the active region of a *p-n* $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ multiple quantum well heterostructure (QWH) grown lattice matched to a GaAs substrate via metalorganic chemical vapor deposition (MOCVD). The active region consists of four 200 Å (L_z) quantum wells ($x\sim0.2$) separated by three 100 Å (L_B) barriers ($x\sim0.5$), with symmetric upper (*p*-type) and lower (*n*-type) linearly graded ($x\sim0.9$–0.5) confinement layers.

[a] Kodak Doctoral Fellow.

Damaged and damage-free hydrogenation of GaAs: The effect of reactor geometry

Ref. 16

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The effects on GaAs hydrogenation of two different rf reactor types are investigated, one a parallel-plate reactor with a capacitively coupled discharge and the other an inductively coupled system. The atomic hydrogen, dissociated in the plasma of either system, passivates impurities in GaAs. The plasma in the capacitively coupled discharge reactor develops a large self-bias relative to the sample and large ion energies (~ 100 eV), resulting in significant etching of the GaAs surface. In spite of the surface erosion, passivation of donors by hydrogen diffusing into the material is observed. The sample hydrogenated in the inductively coupled discharge ($kT_e/q < 1$–2 eV) is not etched, exhibiting, nevertheless, a comparable passivation of donors. Hydrogenation without surface damage is accomplished with the sample in the glow discharge of an inductively coupled reactor but not in a capacitively coupled discharge.

I. INTRODUCTION

The effects of incorporating atomic hydrogen into GaAs have recently been documented. Among the effects investigated is the tendency for atomic hydrogen to passivate shallow-donor levels[1,2] and acceptor levels[3,4] in GaAs. Also observed is a reduction in the concentration of deep levels.[5] The passivation of acceptors, particularly in $Al_xGa_{1-x}As$, creates resistive material which, of course, has technological importance. By masking the hydrogenation process with SiO_2, we are able to demonstrate stripe-geometry gain-guided lasers in the $Al_xGa_{1-x}As$-GaAs system.[6,7]

To introduce the atomic hydrogen into the material, the sample is placed within a vacuum chamber and a hydrogen plasma is generated. A common geometry used is a parallel-plate arrangement where the rf power is capacitively coupled to the plasma.[1,2,6] The sample is placed on the grounded electrode. In the parallel-plate geometry, the grounded electrode acts as the cathode for one-half the rf cycle, and in the absence of a self-bias on the driven electrode the accompanying cathode sheath is equal in magnitude to the peak rf voltage. Of course, a dc bias forms on the driven electrode and, as a consequence, the cathode sheath at the grounded electrode is less than one-half of the peak-to-peak rf voltage. Despite this fact, the kinetic energy acquired by the H^+ ions accelerated across the sheath towards the grounded electrode is significant. The collisions between the high-energy H^+ ions and the GaAs sample lead to some damage of the GaAs surface.[6] The directed motion of ions is useful if crystal etching is desired, particularly in reactive ion etching; however, the ions are not necessary, nor is etching desired, in the hydrogen passivation process. In some reports precautions have been taken to remove the sample from the discharge to avoid the damage by ion bombardment and the UV radiation of the discharge.[3]

We have experimented with hydrogenation of GaAs using an inductively coupled discharge. One intent has been to maintain a high degree of passivation while eliminating the surface damage that is incurred using the parallel-plate arrangement. The means by which an inductively coupled discharge is sustained leads to a high percent dissociation of molecular hydrogen, making available an abundance of atomic hydrogen to neutralize the dopant sites in GaAs. The high-voltage sheath inherent in the parallel-plate arrangement is eliminated in an inductively coupled discharge. Therefore, hydrogenation of GaAs in an inductively coupled discharge can be performed while preserving the original crystal surface topology.

II. EXPERIMENT

The extent and depth to which the dopants in the crystal are passivated using the two discharge configurations is examined using both n-type GaAs ($n_{Ge} = 1.2\times10^{17}$ cm^{-3}) and p-type GaAs ($n_{Mg} = 10^{18}$ cm^{-3}). The samples are maintained at a temperature of 250 °C during a 10-min plasma exposure. Capacitance versus voltage (C-V) measurements are performed to determine the free-carrier concentration in the GaAs both before and after plasma exposure. The decrease in the free-carrier concentration gives an indication of the efficiency of the hydrogenation process in the two discharge arrangements.

To determine the amount of crystal etching that occurs on exposure to the discharge arrangements, samples consisting of 1-μm-thick layers of GaAs separated by layers of $Al_xGa_{1-x}As$ are used. The $Al_xGa_{1-x}As$ layers serve as convenient "markers." By comparing the thickness of the surface layer of GaAs after exposure to the plasma to the thickness of the unexposed GaAs layers, we determine how much of the surface GaAs layer has been etched. In this way, a scanning electron microscope (SEM) micrograph of the samples after exposure to the plasma yields an accurate measure of the GaAs etch rate. The dependence of the etch rate on sample temperature is measured by performing the hy-

Comparison of Si_{III}-Si_V and Si_{III}-V_{III} diffusion models in III-V heterostructures lattice matched to GaAs

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The diffusion of Si_{III}-Si_V neutral pairs versus the diffusion of Si_{III}-V_{III} complexes in III-V crystals is compared in the light of experimental data showing the effect of Si diffusion on self-diffusion of column III and column V lattice atoms. Secondary-ion mass spectroscopy is used to compare the enhanced diffusion of column III or column V atoms in several different Si-diffused heterostructures closely lattice matched to GaAs. Enhancement of the lattice-atom self-diffusion, via impurity diffusion, is found to occur predominantly on the column III lattice. Supporting the Si_{III}-V_{III} diffusion model, these data indicate that the main native defects accompanying the Si diffusion are column III vacancies, which diffuse directly on the column III sublattice.

Impurity-induced layer disordering (IILD) in III-V heterostructures[1] has attracted interest not only for reasons of device fabrication but also for fundamental studies of impurity diffusion, self-diffusion, and crystal defects. Although the effects of many different impurities in IILD have been investigated, Si has been found to be the most versatile and effective in layer intermixing. It has been studied as a diffusant from the crystal surface,[2] as an implanted impurity,[3] and as a grown-in dopant.[4] In spite of the many studies of IILD and also the role of Si in III-V diffusion processes, uncertainty remains as to the crystal mechanisms that govern these processes. Greiner and Gibbons have proposed that the Si impurity diffuses in GaAs, and presumably in $Al_xGa_{1-x}As$, as nearest neighbor neutral pairs, i.e., as Si_{Ga}-Si_{As}.[5] This model was proposed before it was known that the Si impurity causes layer intermixing when diffused into $Al_xGa_{1-x}As$-GaAs quantum well heterostructures (QWHs).[2] Although it has been shown that Si diffusion must occur in the QWH for layer intermixing to take place,[4] a detailed mechanism of how the Si_{III}-Si_V pair might cause the layer disordering has not been proposed. In spite of this, the Greiner and Gibbons neutral pair Si diffusion model has found widespread acceptance.[6-10]

A second diffusion model proposed by some of the present authors maintains that the Si impurity diffuses as a complex of a Si donor and a column III vacancy, i.e., as Si_{III}-V_{III}.[11-13] Although the model is consistent with the available experimental data involving both Si diffusion and the layer intermixing, additional experimental data characterizing both the Si diffusion and its effect on the III-V crystal self-diffusion would be helpful. In this letter we present experimental data on the effect of Si diffusion on column III *and on column V* lattice atom self-diffusion in III-V heterostructures that are closely lattice matched to GaAs. We relate these data to proposed models of both IILD and Si diffusion in GaAs.

The crystals used in this study have been grown on (100) GaAs substrates using metalorganic chemical vapor deposition. Three different heterostructures are used. The first is an undoped superlattice (SL) consisting of 36 periods of the four layers AlAs(60 Å)-$Al_{0.2}Ga_{0.8}As_{0.95}P_{0.05}$ (185 Å)-AlAs(60 Å)-GaAs (190 Å). The second wafer is a lattice-matched $In_{0.2}Ga_{0.8}As_{0.5}P_{0.5}$-GaAs heterojunction in which the $In_{0.2}Ga_{0.8}As_{0.5}P_{0.5}$ epitaxial layer is ~0.7 μm thick. The third crystal is an $In_{0.5}Al_{0.2}Ga_{0.3}P$-GaAs heterojunction. Silicon diffusion into these crystals has been performed in sealed quartz ampoules with excess vapor pressures of a combination of As and P. The diffusion source consists of an elemental layer of Si (~200 Å) deposited on the crystal surface. The heterostructures are analyzed using secondary-ion mass spectroscopy (SIMS).

Figure 1 shows SIMS profiles of the Al and P for the 36 period SL for both the as-grown crystal, Fig. 1(a), and after Si diffusion for 9 h at 800 °C, Fig. 1(b), in which the Si diffuses about halfway through the SL. Profiles of the SL that has been simply thermally annealed (no Si diffusion) for 12 h at 825 °C (data not shown) remain almost identical to those of the as-grown crystal, Fig. 1(a). This verifies that the change in the Al and P profiles (the layer interdiffusion) seen in Fig. 1(b) is in fact brought about by the Si diffusion in these layers. Note that while the Si diffusion totally intermixes the column III lattice atoms Al and Ga [the Ga not shown in Fig. 1(b)] as expected from previous experiments,[2] considerable modulation remains for the column V atoms (As and P) as is evident from the P profile. An accurate comparison between the amount of interdiffusion for the two sublattices is difficult to make in this structure.

Figure 2 shows SIMS data on a second crystal, an $In_{0.2}Ga_{0.8}As_{0.5}P_{0.5}$-GaAs heterojunction. Figure 2(a) shows profiles of the lattice constituents after a simple thermal anneal of 6 h at 850 °C, while Fig. 2(b) shows profiles for the heterojunction after Si diffusion for 6 h at 850 °C. Obvious in Fig. 2(b) is the major enhancement in the In diffusion into the GaAs substrate crystal and the smoothing

Atom diffusion and impurity-induced layer disordering in quantum well III-V semiconductor heterostructures

Ref. 18

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The process of impurity-induced layer disordering (IILD) or layer intermixing, in $Al_xGa_{1-x}As$-GaAs quantum well heterostructures (QWHs) and superlattices (SLs), and in related III-V quantum well heterostructures, has developed extensively and is reviewed. A large variety of experimental data on IILD are discussed and provide newer information and further perspective on crystal self-diffusion, impurity diffusion, and also the important defect mechanisms that control diffusion in $Al_xGa_{1-x}As$-GaAs, and in related III-V semiconductors. Based on the behavior of Column III vacancies and Column III interstitials, models for the crystal self-diffusion and impurity diffusion that describe IILD are reviewed and discussed. Because impurity-induced layer disordering has proved to be an important method for III-V quantum well heterostructure device fabrication, we also review the application of IILD to several different laser diode structures, as well as to passive waveguides. We mention that it may be possible to realize even more advanced device structures using IILD, for example, quantum well wires or quantum well boxes. These will require an even greater understanding of the mechanisms (crystal processes) that control IILD, as well as require more refined methods of pattern definition, masking procedures, and crystal processing.

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I. INTRODUCTION

Since the discovery of impurity-induced layer disordering (IILD) in 1980 by Laidig *et al.*[1] in an attempt to modify undoped $Al_xGa_{1-x}As$-GaAs superlattices (SLs) to doped SLs (for phonon experiments),[2] there has been a growing research effort to understand disordering mechanisms, to understand the crystal and defect diffusion processes inherent in layer disordering, and to utilize the IILD process for device fabrication. Laidig *et al.*[1] found that the layers of an AlAs-GaAs superlattice (SL) are unstable against Zn diffusion and intermix, thus yielding bulk, undamaged, homogeneous material of an Al composition average to that of the original SL. This process occurs at temperatures much less than those necessary for ordinary thermal interdiffusion of the layers of an undoped SL,[3] which, of course, makes IILD especially interesting and important. Since the Zn diffusion can easily be masked at the crystal surface, as in Fig. 1, the impurity-induced layer disordering allows desired regions of quantum well heterostructures (QWHs) to be altered in effective energy gap and refractive index.[4] Figure 2 shows the energy shift directly (in this case a visual color shift) for selective IILD via Si diffusion in an $Al_{0.6}Ga_{0.4}As$-GaAs SL.[5] The IILD is performed in a dot pattern, as might be important in forming an array of quantum well (QW) "dots," and visible spectrum light is transmitted through disordered portions of the crystal. Regions where IILD has shifted the effective energy gap to higher energies appear red, a true color shift, while other areas of the crystal appear dark due to QW band-to-band absorption of the visible spectrum light in the intact SL.

Based on the results of Ref. 1, it was appreciated immediately that impurity implantation, specifically Si implantation (with subsequent annealing of damage), could be used to intermix $Al_xGa_{1-x}As$-GaAs heteroboundaries and layers.[6] Besides the success of Si implantation,[6,7] Camras *et al.*[8] showed that the Zn impurity also could cause disordering when implanted into an $Al_xGa_{1-x}As$-GaAs SL that is then annealed to remove damage. Since this early work,[1-8] many different methods and impurities (or defects) have been found to effect IILD and the selective intermixing of III-V QWHs or SLs. Several different impurities such as the donors Si,[5,9] Ge,[10] S,[11] Sn,[12] and Se,[13] as well as the acceptors Zn,[1] Be,[14] and Mg,[13] have been found to cause layer intermixing either when diffused into the QWH, or during post-growth annealing for the case when the impurities are grown into the crystal. Gavrilovic *et al.*[15] showed that layer intermixing could result from the annealing of lattice damage due to ion implantation. The ion implantation of many different atomic species (not necessarily dopants)[6] has been found to induce layer intermixing.[15-18] In addition, Epler *et al.*[19] have shown that laser melting can be used to incorporate (selectively) Si to a shallow depth in an $Al_xGa_{1-x}As$-GaAs

Ref. 19

Column III and V ordering in InGaAsP and GaAsP grown on GaAs by metalorganic chemical vapor deposition

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Data are presented showing that $GaAs_{1-y}P_y$ grown on GaAs by metalorganic chemical vapor deposition (MOCVD) at relatively low temperature ($\sim$640 °C) exhibits ordering on the column V sublattice. These data, with electron diffraction data and impurity-induced layer disordering data, show that column III site and column V site ordering is possible for the quaternary InGaAsP grown on GaAs by MOCVD at relatively low temperature ($\sim$640 °C). Ordered InGaAsP grown on GaAs shifts in photoluminescence wavelength $\sim$130 meV higher in energy with disordering by annealing or by impurity-induced intermixing.

Since the first reports of ordering in III-V semiconductors, specifically in the ternary AlGaAs,[1] ordering has been observed in many other III-V ternary alloys.[2-4] Mainly the ordering occurs on the column III sublattice, but only for the case of GaAsSb lattice matched to InP has it been observed on the column V site.[5] Column III ordering has also been observed in the quaternary alloy InGaAsP grown on InP substrates.[6] In the quaternary alloy the interesting possibility exists of both sublattices being ordered. We present data indicating that this possibility may indeed be the case for InGaAsP layers grown lattice matched to GaAs at relatively low temperature ($\sim$640 °C) by metalorganic chemical vapor deposition (MOCVD).[7] To show that As-P (column V) ordering in III-V alloys can occur, we also present data showing ordering in the GaAsP ternary alloy, which, incidentally, is an old problem.[8]

Showing that the column V site is ordered in InGaAsP is at best a difficult task because it is not obvious how to distinguish clearly the difference between the column V and column III electron diffraction patterns, which in the present work are obtained via transmission electron microscopy (TEM). In order to show that column V site ordering is possible (As and P ordering), it is necessary to remove the ambiguity between column III and column V ordering. Since there is no column III ordering possible in the ternary GaAsP, we have decided first to check this alloy grown on GaAs and see if it exhibits any ordering phenomena.

Figure 1 shows electron diffraction patterns for a (110) cross section of (a) an $In_{1-x}Ga_xAs_yP_{1-y}$ ($x\sim0.75$, $y\sim0.45$) epilayer and (b) a $GaAs_{1-x}P_x$ ($x\sim0.55$) epilayer. Both layers are grown via MOCVD in an Emcore GS 3000 DFM reactor on GaAs substrates. The epitaxial layer growths are carried out at 100 Torr at a temperature of 640 °C. The growth rate is 1 μm/h and the V/III ratio is $\sim$150. The two sets of extra diffraction spots seen in Fig. 1(b) clearly show ordering of the column V site. This diffraction pattern is very different from the pattern observed for GaAsSb grown on InP,[5] indicating a different type of column V ordering is present for GaAsP grown on GaAs. The diffraction pattern for the InGaAsP layer [Fig. 1(a)] is nearly identical to the pattern for the GaAsP with, however, two major exceptions. First, the intensity of the extra spots is much stronger throughout the entire sample. Second, the brightest set of extra spots is clearly skewed in the $[1\bar{1}5]$ direction as indicated by the alignment marks [Fig. 1(a)] around the 1/2 $1\bar{1}1$ satellite diffraction spot. In contrast, the 1/2 $1\bar{1}1$ spot on the GaAsP diffraction pattern is not skewed. In Fig. 2(a) the InGaAsP image (TEM cross section) is formed by using the skewed 1/2 $1\bar{1}1$ spot with the g vector indicated, and antiphase boundaries of the ordered quaternary normal to the $[1\bar{1}5]$ direction (small arrow) are clearly evident. The as-grown InGaAsP [Fig. 2(a)] can be viewed as a pseudosuperlattice, and, of course, will change its effective energy gap if it then is disordered.[9]

Recently it has been shown that Zn diffusion into ordered InGaP will cause the structure to become the random alloy[10] in the same way as Zn diffusion into an AlAs-GaAs superlattice will cause the layers to intermix and disorder.[9] In both cases the Zn diffusion eliminates the atomic order on the column III lattice sites, with an undetermined effect on the column V lattice sites. In contrast, recent work on Zn diffusion into InAlGaP-GaAs heterolayers indicates that the column V site is relatively "untouched" (unaffected) by Zn diffusion.[11] If this behavior is general, Zn diffusion into a

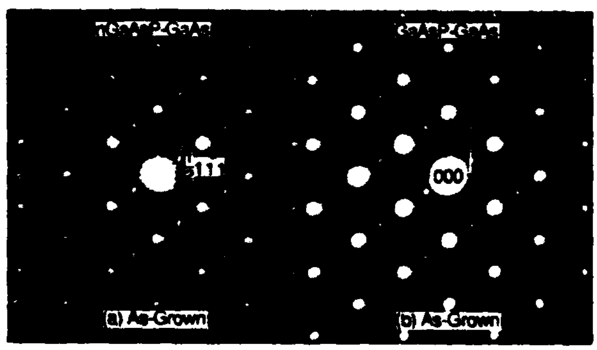

FIG. 1. Diffraction patterns on (110) cross sections for (a) InGaAsP and (b) GaAsP epitaxial layers grown on (100) GaAs substrates by MOCVD. The 1/2 $1\bar{1}1$ sattelite diffraction spot of (a) is skewed along the $[1\bar{1}5]$ direction.

[a] Kodak Doctoral Fellow.

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STIMULATED EMISSION IN $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ QUANTUM WELL HETEROSTRUCTURES

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For shorter wavelength lasers ($\lambda < 600$ nm), the most prospective III–V alloy system is $In_{1-y}Ga_yP$ lattice matched to GaAs ($y \sim 0.5$) and its variant, the case of Al–Ga substitution, $In_{0.5}(Al_xGa_{1-x})_{0.5}P$. We report the growth of quantum well heterostructures (QWHs) in this system by metalorganic vapor phase epitaxy and the photopumped (77 K) laser operation of InAlGaP QWHs at wavelengths ranging from the orange to the green portions of the spectrum. Continuous wave (CW) photopumped laser operation at 77 K is achieved in the range from ~ 570.0 to ~ 550.0 nm (2.175 to 2.254 eV), and pulsed operation to wavelengths as short as 543.0 nm (2.283 eV). Room temperature pulsed laser operation is demonstrated in the range from ~ 610.0 to 590.0 nm (2.032 to 2.101 eV). The shortest lasing wavelengths observed at 77 K (543.0 nm pulsed and 553.0 nm CW) and at 300 K (593.0 nm pulsed and 625.0 nm CW) represent the highest energy lasers yet reported for this material system, or for any III–V alloy system. This paper will describe the epitaxial layers grown, the characterization of these layers using a variety of techniques, including TEM, and the laser operation experiments and results.

1. Introduction

The quaternary alloy $In_{0.5}(Al_xGa_{1-x})_{0.5}P$ is the most prospective material for short wavelength ($\lambda < 600$ nm) visible lasers and light emitting diodes, owing to its large direct bandgap energy (up to 2.26 eV) and its ability to form high efficiency double heterostructure (DH) devices lattice matched to a GaAs substrate. Because of the thermodynamic stability of AlP relative to InP, metalorganic vapor phase epitaxy (MOVPE), one of the kinetically-controlled growth processes, was anticipated to become a very useful technique for the growth of InAlGaP [1]. To date, after extensive research efforts, high quality materials have been successfully grown by both atmospheric [2–4] and low pressure [5–7] MOVPE. Room temperature CW operation of InGaP/InAlGaP DH laser diodes has been reported by several groups [4–6]. The emission wavelengths of these red lasers were between 670 and 690 nm. Investigations of single [8] or multiple [9] quantum well heterostructures (QWHs) with InGaP active layers have resulted in somewhat reduced (~ 660 nm) emission wavelength.

In order to produce lasers emitting in the orange (~ 620 nm) and yellow (~ 580 nm) portions of the visible spectrum, and, more importantly, to study the short wavelength limit of this material system, it is necessary to grow a high quality $In_{0.5}(Al_xGa_{1-x})_{0.5}$ P quaternary active layer with high aluminum composition ($0.2 < x < 0.6$). Efforts so far have yielded pulsed [10] and CW [11] 77 K laser operation at around 580 nm ($x \sim 0.3$) and pulsed 300 K laser operation at 626.2 nm ($x \sim 0.17$) [12].

One of the major difficulties cited in these studies for reducing laser emission wavelength is

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DISORDERING OF THE ORDERED STRUCTURE IN MOCVD-GROWN GaInP AND AlGaInP BY IMPURITY DIFFUSION AND THERMAL ANNEALING

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$Ga_{0.5}In_{0.5}P$ and $(Al_xGa_{1-x})_{0.5}In_{0.5}P$ grown by metal-organic chemical vapor deposition (MOCVD) at temperatures below 700 °C show an ordered arrangement of the group III atoms on the column III sublattice. A periodic compositional modulation along the growth direction is also observed under certain growth conditions. This paper presents data showing that epitaxial layers of both $Ga_{0.5}In_{0.5}P$ and $(Al_xGa_{1-x})_{0.5}In_{0.5}P$ grown on (001) GaAs substrates and containing the ordered phase can be converted to disordered alloys by thermal annealing under a variety of conditions at temperatures not exceeding the growth temperature. The disappearance of the ordered phase, as determined by TEM, is accompanied by a shift of the bandgap to higher energy by ≈ 90 meV. $Ga_{0.5}In_{0.5}P$ and $(Al_xGa_{1-x})_{0.5}In_{0.5}P$ have been annealed in sealed ampoules under the following conditions: (1) thermal anneal with P_4 overpressure, (2) Zn diffusion with Zn_3P_2 only, and (3) Zn diffusion with both Zn_3P_2 and P_4. Similar bandgap shifts are obtained under all three conditions. It is further shown that selective disordering with either Zn or P_4 can be achieved by using a patterned dielectric mask. The relative stabilities of the random and the ordered alloys are discussed in light of these disordering data.

1. Introduction

The bandgap energy (E_g) of $Ga_{0.5}In_{0.5}P$ grown lattice-matched on (001) GaAs substrates by metalorganic chemical vapor deposition (MOCVD) has been found to be lower than that of crystals grown by liquid phase epitaxy (LPE) by more than 50 meV, depending on the growth conditions, i.e., the growth temperature and the V/III ratio in the gas phase [1–5]. At the same time, transmission electron microscopy (TEM) studies of $Ga_{0.5}In_{0.5}P$ grown by MOCVD at temperatures below 700 °C reveal an anomalous diffraction pattern [6–8] in the ⟨110⟩ orientation, with additional strong extra spots halfway between the diffraction spots from the zinc blende (ZB) matrix, suggesting a preferential ordering of the In and Ga atoms on the column III sublattice. No additional diffraction spots were observed in the orthogonal ⟨1$\bar{1}$0⟩ orientation. The ordered structure was found to be trigonal with In–Ga ordering occurring on {111} planes [6,7]. $Ga_{0.5}In_{0.5}P$ grown by MOCVD at 700 °C, on the other hand, exhibits a diffraction pattern of only the ZB matrix, indicating a nearly random arrangement of In and Ga atoms on the column III sublattice, and has a band gap coinciding with that of LPE-grown crystals [2].

Recently, it has been shown by TEM and photoluminescence (PL) [7] that Zn diffusion from a Zn_3P_2 source converts the ordered distribution of Ga and In atoms on the column III sublattice in as-grown $Ga_{0.5}In_{0.5}P$ to a random alloy, with a simultaneous shift of E_g to higher energy by ≈ 90 meV. In the present work we extend these studies to the quaternary alloy $(Al_xGa_{1-x})_{0.5}In_{0.5}P$, which

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DEPTH-DEPENDENT NATIVE-DEFECT-INDUCED LAYER DISORDERING IN $Al_xGa_{1-x}As$-GaAs QUANTUM WELL HETEROSTRUCTURES

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Abstract

Photoluminescence measurements on annealed single-well $Al_xGa_{1-x}As$-GaAs quantum-well heterostructures demonstrate that layer disordering caused by native defects is strongly depth dependent. The depth-dependent layer disordering, as well as the corresponding depth-dependent net carrier concentration, is a consequence of the re-equilibration of the V_{Ga}^- vacancy and the As_{Ga}^+ anti-site native defect concentrations via the crystal surface.

HYDROGENATION AND SUBSEQUENT HYDROGEN ANNEALING OF GaAs ON Si

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The effects of hydrogenation and subsequent annealing on unintentionally doped GaAs layers grown directly on Si substrates by metalorganic chemical vapor deposition have been characterized by capacitance-voltage measurements, Hall effect measurements, transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). Significant reduction of the carrier concentration in the GaAs layers after hydrogen plasma exposure is obtained. TEM shows that the hydrogen plasma slightly etches the surface of the GaAs layers, and EDS demonstrates that the etched area becomes arsenic deficient and contains minute Ga particles. In addition, atomic hydrogen diffuses deeply along threading dislocations and microtwin interfaces into the GaAs layers and reacts with GaAs locally around the defects.

Role of Native Defects in Al-Ga Interchange and Layer Disordering in $Al_xGa_{1-x}As$ Quantum Well Heterostructures

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ABSTRACT: Data are presented demonstrating the effects of growth parameters (Fermi-level and V/III ratio) and annealing conditions (surface encapsulants and As_4 pressure) on Al-Ga interdiffusion in MOCVD grown $Al_xGa_{1-x}As$-GaAs QWHs.

1. INTRODUCTION

As suggested by Laidig et al (1981), impurity-induced layer disordering (IILD) has important consequences for fabrication of thin layer $Al_xGa_{1-x}As$-GaAs buried heterostructure devices. In order to realize fully the potential of IILD it is necessary to better understand the Al-Ga interchange mechanism. In the experiments described here $Al_xGa_{1-x}As$-GaAs superlattices (SLs) and single-well quantum well heterostructures (QWHs) grown by metalorganic chemical vapor deposition (MOCVD) are used to study Al-Ga interdiffusion. Photoluminescence (PL), transmission electron microscopy (TEM), and secondary ion mass spectroscopy (SIMS) data show that the crystal surface condition (surface encapsulant and As_4 pressure) strongly influences Al-Ga interdiffusion. For a clearly defined Al-Ga interdiffusion regime we have measured the activation energy for Al-Ga interchange (E_{Al-Ga}), thereby labeling this regime. By employing three single-well QWHs that differ only in the QW location, we further demonstrate that Al-Ga interchange is enhanced by re-equilibration of depth-dependent native defect concentrations involving the crystal surface. In contrast PL and TEM measurements of annealed $Al_xGa_{1-x}As$-GaAs SLs show that Al-Ga interdiffusion is relatively depth-independent. Finally, we have investigated the effect of crystal growth parameters (Fermi-level and V/III gas ratio) on the Al-Ga interchange mechanism.

2. EXPERIMENTAL RESULTS

2.1 Activation Energy

To the extent that the activation energy varies with growth parameters and experimentally determined annealing-conditions values of E_{Al-Ga} can ultimately be used to label interdiffusion regimes. Consequently, the magnitude of E_{Al-Ga} will provide insight to the atomic mechanisms responsible for Al-Ga interchange. A review of available Al-Ga interdiffusion data (Figure 1) reveals considerable disagreement in reported values of E_{Al-Ga}. Some significant trends emerge after correcting these data for

CW Room Temperature Operation (<640 nm) of AlGaInP Multi-Quantum-Well Lasers

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ABSTRACT: We recently demonstrated pulsed room temperature diode laser operation at 625 nm in OMVPE-grown single-quantum-well heterostructures. Improved device performance has now been achieved with multi-quantum-well graded-index separate-confinement heterostructures. The best laser diodes have operated CW at room temperature at wavelengths less than 640 nm with threshold current densities as low as 3.7 kA/cm^2. The growth, structure, and operating characteristics of these multi-quantum-well devices will be described.

1. INTRODUCTION

Interest in short-wavelength semiconductor lasers has grown considerably in recent years with the progress that has been made in the AlGaInP alloy system (Bour et al, 1987, Fujii et al, 1987, Ikeda et al, 1987, and Ishikawa et al, 1987). Already, double heterostructure lasers using a GaInP active layer operating in the 670-680 nm wavelength range are becoming commercially available. Shorter wavelength operation is desirable, however, for such applications as bar-code scanners, laser printers, and high-density optical storage media. In order to achieve lasing wavelengths much below 650 nm at room temperature, it is necessary to use an AlGaInP active layer in the device structure. Kawata et al (1987) described room temperature CW lasing at 640 nm with a double heterostructure using an AlGaInP active region, and even shorter wavelength operation has been achieved in pulsed mode and at reduced temperatures (Nam et al, 1988, Kuo et al, 1988, and Kawata et al, 1986). We now report the room temperature CW operation of AlGaInP lasers using multi-quantum-wells in a graded-index separate-confinement heterostructure (GRINSCH). Lasing at wavelengths less than 640 nm has been achieved with threshold current densities of 3.7 kA/cm^2 or below, the lowest reported to date. Although several different device structures have been grown, including conventional double heterostructures and single-quantum-wells, the four-well structure described here has been found to perform the best at this time.

OBSERVATION OF PHONON-ASSISTED LASER OPERATION OF $Al_xGa_{1-x}As$-GaAs QUANTUM WELL HETEROSTRUCTURES

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Data are presented showing that the key to observing the phonon-assisted photopumped laser operation of narrow rectangular samples of $Al_xGa_{1-x}As$-GaAs quantum well heterostructures (QWH's) is the control of the edge-to-edge resonator Q across the sample. If the sample is heat sunk in metal, with metal reflectors folded upward along the edges, the resonator Q across the sample is high, and laser operation across the sample on confined-particle states (a reference) and along the sample a phonon lower in energy ($\Delta E \approx \hbar\omega_{LO}$) is observed. If the sample edges across the sample are left uncoated (weakly reflecting, low Q), laser operation is observed only along the sample (longitudinal modes) but shifted ($\Delta E \approx \hbar\omega_{LO}$) below the confined-particle states and absorption. A QWH rectangle, with proper heat sinking and control of its edge-to-edge resonator Q, can act as a hot phonon "spectrometer" if it is fully photopumped across its width and is only partially pumped along its length.

DISORDER-DEFINED BURIED HETEROSTRUCTURE $Al_xGa_{1-x}As$-GaAs QUANTUM WELL LASERS BY DIFFUSION OF SILICON AND OXYGEN FROM Al-REDUCED SiO_2

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Abstract

We describe a convenient method utilizing chemical reduction of SiO_2 by Al (from $Al_xGa_{1-x}As$) to generate Si and O for impurity-induced layer disordering (IILD) of $Al_xGa_{1-x}As$-GaAs quantum well heterostructures (QWHs). Experimental data show that Si-O diffusion (from SiO_2) is an effective source of Si for Si-IILD and of O that compensates the Si donor, thus resulting in higher resistivity layer-disordered crystal. The usefulness of the Si-O IILD source for fabricating low threshold disorder-defined buried heterostructure $Al_xGa_{1-x}As$-GaAs QWH lasers is demonstrated.